

*Vol. 22, No. 1, January-February, 1987*

September, 1987

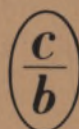
LTMRAR 22(1) 1-108 (1987)

# **LITHOLOGY AND MINERAL RESOURCES**

**ЛИТОЛОГИЯ И ПОЛЕЗНЫЕ ИСКОПАЕМЫЕ**

**(LITOLOGIYA I POLEZNYE ISKOPAEMYE)**

**TRANSLATED FROM RUSSIAN**



**CONSULTANTS BUREAU, NEW YORK**

# LITHOLOGY AND MINERAL RESOURCES

*Lithology and Mineral Resources* is abstracted or indexed in *Chemical Abstracts*, *Engineering Index*, and *Metal Abstracts Index*.

Mailed in the USA by Publications Expediting, Inc., 200 Meacham Avenue, Elmont, NY 11003.

**POSTMASTER:** Send address changes to *Lithology and Mineral Resources*, Plenum Publishing Corporation, 233 Spring Street, New York, NY 10013.

*Lithology and Mineral Resources* is a translation of *Litologiya i Poleznye Iskopaemye*, a publication of the Academy of Sciences of the USSR.

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233 Spring Street  
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Published bimonthly, consisting of Volume 21 issues 3 through 6 and Volume 22 issues 1 and 2. Subscription price for Volume 21 is \$645, and for Volume 22 \$715. Second-class postage paid at Jamaica, New York 11431.

# LITHOLOGY AND MINERAL RESOURCES

A translation of *Litologiya i Poleznye Iskopaemye*

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Volume 22, Number 1

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*The Russian press date (podpisano k pechaty) of this issue was 1/22/1987.  
Publication therefore did not occur prior to this date, but must be assumed  
to have taken place reasonably soon thereafter.*

Correlations are constructed of the occurrence areas of climatic complexes of planktonic foraminifers, latitudinal facies zones of deep-sea sediments, and surface water masses in the Recent world ocean and in various stages of the latest continental glaciation in the Northern Hemisphere; it is concluded that latitudinal facies zones migrate depending on the global climate. The variation is described of the depth position of critical levels of  $\text{CaCO}_3$  dissolution as related with the stages of the Late Quaternary glaciation. The Late Quaternary facies of the Red Sea are examined, showing that the drastic changes in sedimentation settings of this basin were caused by glacioeustatic fluctuations of the ocean level.

Global climatic change and glacioeustatic fluctuations of the world ocean level due to the latest (Würm and Wisconsin) continental glaciations in the Northern Hemisphere are known to have caused drastic restructurings of shallow sea facies settings. The influence of glaciation on deep-sea marine and oceanic facies, especially in regions remote from continental ice sheets, is less clear. These events, as documented by deep-sea sediment columns, have been mainly deciphered by micropaleontological and isotopic-oxygen methods [10, 14, 30, 45, 47]. Most investigations did not include an analysis of the genesis of sedimentary facies. Reconstructions of deep-sea facies settings for the individual stages in Late Quaternary history of the oceans were also hampered by the existence of detailed globally correlated stratigraphic scales. Such scales (isotopic-oxygen and climate-stratigraphic) have been developed only for carbonate (foraminiferal) sediments [27, 28, 32, 36, 42].

This investigation examines the response of deep-sea facies systems of the ocean and the semiclosed Red Sea to global change of natural environments caused by the latest glaciation in the Northern Hemisphere and some of its stages. Taking the Recent system of deep-sea facies as an actualistic model [15, 16], we have examined the facies of the deep-sea sediments of the various glaciation stages as they differ from Recent facies due to: (a) shifts of the climatic zones; (b) changed environments for the dissolution of biogenic  $\text{CaCO}_3$  on the seafloor; and (c) glacioeustatic fluctuations of the sea level.

#### MIGRATION OF LATITUDINAL FACIES ZONES

Sublatitudinal deep-sea zones of pelagic facies have been established in the Recent ocean which reflect the global climatic zonality of pelagic sedimentogenetic factors, and primarily the conditions of biogenic sedimentation, which are highly sensitive to climate [12, 13, 15, 16]. The latitudinal zonality of biogenic sedimentation is controlled by the zonal distribution of biological productivity [11] and by the biological geography of sediment-forming planktonic organisms, such as foraminifers, coccolithophores, diatoms, radiolarians, and others. Globally, the structure of the field of primary production is reflected in latitudinal facies zones. The equatorial zone and the two temperate humid zones, characterized by heightened primary production, correspond to latitudinal belts of biogenic silica accumulation and accelerated carbonate and clay accumulation [6, 12, 33]. The centers of subtropical current gyres (the arid zones), situated between these belts, are "ocean deserts" with the lowest biological productivity.

The biogeographical zonality of sediment-forming plankton is controlled by surface water temperature, which is reflected in the latitudinal zonality of thanatocoenoses of planktonic organisms in seafloor sediments [2, 3, 7]. Micropaleontological methods of paleotemperature studies are based on the correlation between the composition of thanatocoenoses of planktonic

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Institute of Oceanology, Academy of Sciences of the USSR, Moscow. Translated from *Litologiya i Poleznye Iskopaemye*, No. 1, pp. 3-16, January-February, 1987. Original article submitted March 24, 1986.



organisms and surface water temperature. It remains, however, largely unclear how the paleotemperature zones established by thanatocoenoses correlate with the facies zones determined by biological productivity.

On the basis of a correlation between the mean annual temperatures of surface waters in Recent oceans and the thanatocoenoses of planktonic foraminifers in the surface layer of pelagic sediments, the following climatic zones have been established [3, 7]: polar ( $4^{\circ}\text{C}$ ), subpolar ( $4-8^{\circ}\text{C}$ ), temperate ( $8-13^{\circ}\text{C}$ ), subtropical ( $13-24^{\circ}\text{C}$ ), tropical ( $24-27^{\circ}\text{C}$ ), and equatorial-tropical ( $26-29^{\circ}\text{C}$ ). Each of these climatic zones corresponds to its specific type of surface water masses, characterized not only by the range of average annual temperatures but also by salinity, content of biogenic elements, biological productivity, and inclusion in a specific macrocirculation system. The water masses and the macrocirculation systems are separated by hydrological fronts, which display increased gradients of the temperature and other hydrologic parameters. On the seafloor, these fronts are reflected in more or less distinct transitions between the latitudinal facies belts. The principal fronts are the boundaries of climatic types of thanatocoenoses of planktonic foraminifers and the climatic zones of the ocean identified by them [7, 18].

The polar zones identified by the absolute predominance of *Globigerina pachyderma* sin correspond to the coldest polar water masses (Arctic and Antarctic). The abundance of ice typical for polar zones is responsible for the prevalence of the facies of terrigenous ice-sea and iceberg sediments [12], which prevail in the high-latitude parts of these zones (in the Arctic Ocean and around Antarctica), which give way to the facies of biogenic silicic or calcareous ooze with scattered material of ice or iceberg transport on the perimeter (the northern part of the Antarctic polar zone north of the Antarctic divergence, and the basins of the Bering and Okhotsk Seas, which according to Stepanov's map [19] are situated north of the Arctic front).

The temperate zones of silicic accumulation thus intrude in their high-latitude peripheral parts into the polar zones (the Arctic and Antarctic water masses), whereas the main portions of these belts occur in high-productivity subpolar (subarctic and subantarctic) types of water masses between the polar and subpolar fronts [19]. Based on planktonic foraminifer thanatocoenoses within these belts, a distinction is made between the subpolar (colder-water) zones and the temperate zone (with warmer water) [1, 2]. The subarctic front in the north and the subantarctic front (often referred to as the subtropic convergence) in the southern ocean separate productive subpolar waters from subtropical waters circulating in subtropical anticyclonic gyres, which have a very low biological productivity. These fronts probably form the natural boundary of the belts of silica accumulation and also the boundaries between the temperate and subtropical thanatocoenoses of planktonic foraminifers. The Arctic and Antarctic fronts and the isotherms of  $8-9^{\circ}\text{C}$  (the nominal boundary between temperate and subpolar thanatocoenoses) apparently are not the limits of silica accumulation belts. The southern polar (antarctic) front, according to Stepanov's map [19], actually lies within the southern silica accumulation belt. A broad transient zone of silicic-carbonate facies occurs between this front and the subantarctic front (above the CCAD [critical carbonate accumulation depth]) and the silicic-clay pelagic sediments; the frontal zone itself is characterized by a high biological productivity.

The subtropical thanatocoenosis is typical for most of the "ocean deserts," although it gives way to warmer-water tropical thanatocoenoses at lower latitudes.

The equatorial productive zone is associated with warm surface water masses rich in nutrients due to the water rising in divergence zones. On the seafloor it is reflected by a latitudinal belt of radiolarian ooze and heightened accumulation rates of calcareous sediments. The latter contain the warmest-water ( $26-29^{\circ}\text{C}$ ) equatorial-tropical thanatocoenoses of planktonic foraminifers, which give way to tropical forms along the perimeter. There is no direct correspondence between the boundaries of the productive zone and the thanatocoenosis. In divergence zones with the highest primary production, surface water temperature is somewhat lower, which is reflected in an increased proportion of cold-water (particularly temperate) species in the thanatocoenoses [7, 10, 18].

The paleotemperature analysis of Late Quaternary columns (0-128,000 years ago) of the calcareous sediments of the Atlantic and Indian Oceans (Fig. 1) identifies surface water paleotemperature fluctuations correlating with isotopic oxygen stages 1-5 and the corresponding phases of the latest continental ice age in the Northern Hemisphere. Most investigators believe that the temperature fluctuations, at least in the higher latitudes, reflect meridional

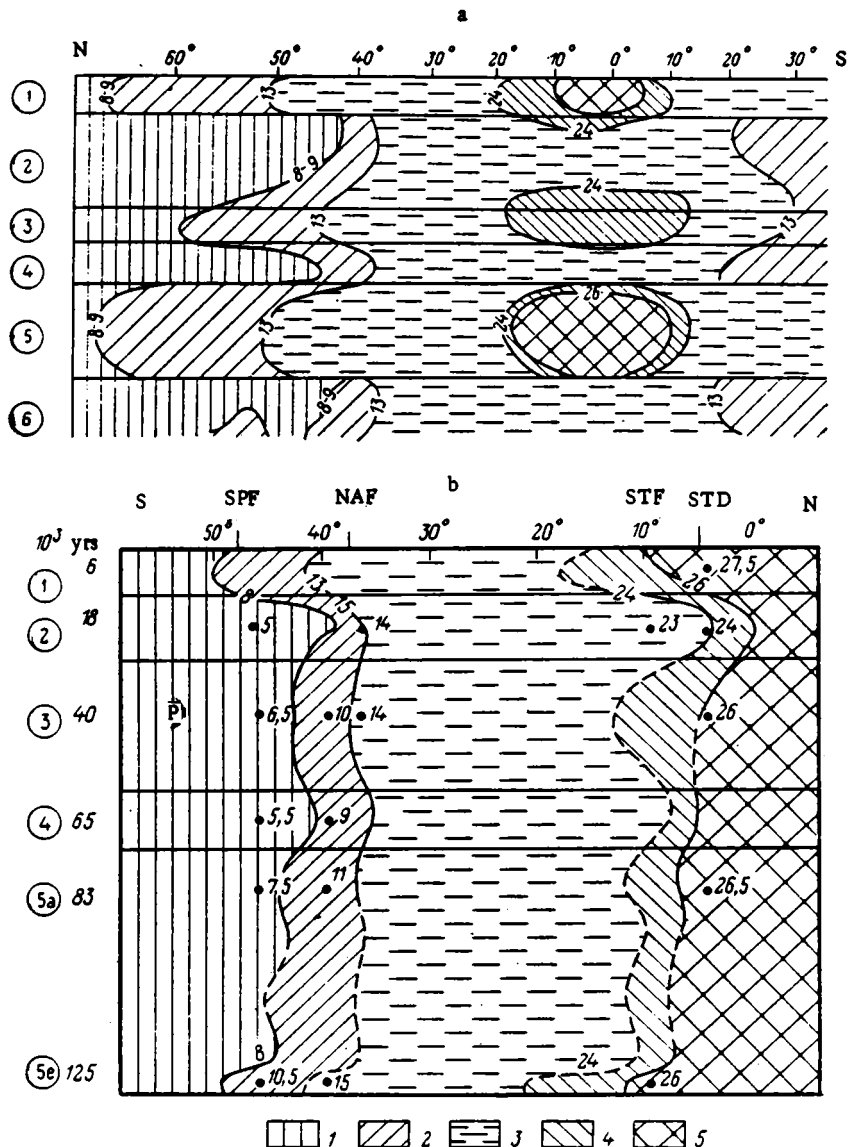


Fig. 1. Migration of climatic zones of the Atlantic (a) [1] and Indian (b) [10, 14, 45, 47] Oceans during the Late Quaternary based on paleotemperature analysis of planktonic foraminifer thanatocoenoses. Climatic zones: (1) subpolar; (2) temperate; (3) subtropical; (4) tropical; (5) equatorial-tropical. Hydrologic fronts: SPF - southern polar front; SAF - subantarctic front; STF - southern tropical front; STD - southern tropical divergence. Numbers indicate paleotemperatures; circled numbers are oxygen isotope stages.

movements of surface water masses and their separating fronts rather than changed properties of these water masses. This is supported by the similarity of the composition of planktonic foraminifer thanatocoenoses of the same type at different horizons of Later Quaternary profiles and that of Recent thanatocoenoses, and also by the similarity of the facies transitions between latitudinal zones, reflecting the position of water masses.

In that case, one should also expect shifts in deep-sea facies and facies transitions coordinated with global climatic oscillations and displacement of water masses [37].

During the latest glaciation (isotope stages 2-4) all the climatic zones as identified by planktonic foraminifer thanatocoenoses were shifted toward the equator to various degrees. The amplitude of this shift decreased from higher to lower latitudes (see Fig. 1). It was

the largest during the latest glacial stage at the peak of the most recent glaciation (oxygen isotope stage 2, some 18,000 years ago), somewhat less in the early stage (stage 4), and weak in the interstadial period (stage 3). The migration of the zones in the Atlantic Ocean [1] was more pronounced than in the Indian Ocean (see Fig. 1). The latter includes the region south of Africa [30, 35] and Australia [46], where the positions of the zones and the fronts separating them were hardly changed.

The ice zones, with their single-type polar thanatocoenoses of planktonic foraminifers, the facies of terrigenous ice-sea and iceberg sediments, coarse clastics of ice transport, and the relatively shallow critical levels of  $\text{CaCO}_3$  dissolution, migrated the farthest (500-1000 km or even more during the glaciation peak) [1, 2, 8, 23-25, 30]. In the Antarctic region, the effect of expansion of the ice zone was apparently intensified by more vigorous turbidity flows during glaciations, which deposited on subcontinental abyssal planes layers of terrigenous turbidities which masked the biogenic sedimentation.

The moderate productive zones (belts of biogenic silica accumulation) were also shifted toward the equator during the cold periods. Their width was reduced, according to several investigators [25, 35, 37], as indirectly supported by the convergence of the polar and subpolar fronts and the narrowing of the temperate thanatocoenosis zone during both stages of the latest glaciation (see Fig. 1). During the interstadial, the temperate zones expanded, probably indicating an expansion of the area of productive surface water and, accordingly, of the silica accumulation belt. According to Lisitsyn [33], however, the width of the southern silica accumulation belt remained practically unaltered.

Judging by the equatorial shift of the subtropical thanatocoenosis boundaries (the subpolar fronts) during cold epochs (isotope stages 2 and 4), the belts of "ocean deserts" were pushed toward lower latitudes by silica accumulation belts, but their centers apparently remained in the same position [25].

During the last ice age, the equatorial zone of high surface water temperatures and the corresponding area of equatorial-tropical thanatocoenosis was somewhat reduced in the Indian Ocean (see Fig. 1b), almost disappeared in the Pacific [17], and is not recorded in the Atlantic at all (see Fig. 1a). During the glacial stages even a tropical temperature zone was absent in the Atlantic Ocean, and the entire subequatorial part of the ocean was occupied by waters which had a temperature of Recent subtropic waters. This does not mean, however, that the equatorial productive zone disappeared completely. More likely, the biological productivity at the equator in cold epochs was even increased by more intense vertical circulation in divergence zones and intensified cold eastern boundary currents and the coastal upwellings associated with them. As water rose more rapidly in divergence areas, the surface water temperatures declined, which was reflected in the greater proportion of cold water species in planktonic foraminifer thanatocoenoses of the equatorial zone [8, 10]. The cooling of the equatorial aquatorium was caused also by an influx of highly productive waters from upwelling zones [2, 35]. The increased bioproductivity during glaciations resulted in a higher organic carbon and lower carbonate content in equatorial sediments [40]. Some of the cores from the equatorial zone of the Atlantic and Pacific registered a heightened  $\text{CaCO}_3$  accumulation rate during the last ice age [22].

As a result of migration of the latitudinal facies belts, zones of cyclic sedimentation developed between them. The cyclic profiles, formed of alternating layers with unequal contents of biogenic silica, are widespread at the margins of silica accumulation belts. The formation of the "silica cycles" can be accounted for by meridional shifts of facies belt boundaries caused by climatic change, which at each point at the belt boundary produced alternations of the conditions of high and low biological productivity. The relevant data for all three silica accumulation zones in the Pacific are given in [3]; for the southern belt of the Indian Ocean the pertinent data have been reported in [46]. Less pronounced "silica cycles" are observed also in the inner parts of silica accumulation belts, where they may be associated both with migrations of maximum bioproductivity zone (the belt axis) and with changed critical depth of  $\text{CaCO}_3$  dissolution (i.e., are associated with carbonate cycles). In each case the cycles correlate with global climatic fluctuations.

#### CHANGED SETTINGS OF $\text{CaCO}_3$ DISSOLUTION AND SHIFTS OF CARBONATE FACIES

Studies of the contemporary processes of biogenic carbonate accumulation conducted mainly in the past two decades revealed a number of more or less pronounced deep levels of variation of the intensity of selective dissolution of the various mineralogic (calcite, aragonite) and

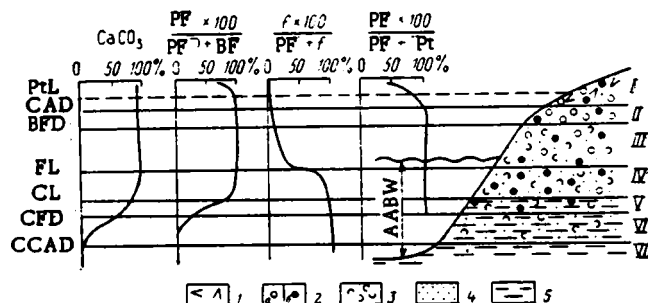


Fig. 2. Facies series of dissolution of pelagic carbonates. Critical dissolution levels: PtL — pteropod lysocline; CAD — critical aragonite depth; BFD — beginning of foraminifer dissolution; FL — foraminifer lysocline; CL — calcite lysocline; CFD — critical depth of planktonic foraminifers; CCAD — critical carbonate accumulation depth. Ratios of numbers in sediments: PF — planktonic foraminifers; BF — benthic foraminifers; Pt — pteropods; f — fragments of planktonic foraminifers. Facies: (I) foraminiferal pteropod; (II) biomorphic foraminiferal; (III) coccolith-foraminifer biomorphic detrital; (IV) foraminiferal nanofossil detrital; (V) foraminiferal nanofossil marly; (VI) nanofossil marly; (VII) carbonate-free pelagic clays or silicic ooze. (1) pteropods; (2) planktonic foraminifera (a — unstable to dissolution; b — stable to dissolution); (3) planktonic foraminifer detritus; (4) nanofossils; (5) clay matter. AABW — Antarctic bottom water.

biomorphic (pteropod and planktonic foraminifer shells, coccoliths) modifications of biogenic calcium carbonate, known as lysoclines and critical depths.

The lysoclines and critical depths separate facies with different degrees of dissolution of planktonogenic  $\text{CaCO}_3$  deposited on the seafloor. The bathymetric position of lysoclines and critical depths varies from one latitudinal zone to another and as a function of the properties of the bottom water masses, sedimentation rates, and a number of other factors [4, 5, 12]. The sequence of critical levels (and, therefore, the facies between them) remains the same, as it is defined by the relative solvability of carbonate components and is determined by a unidirectional trend toward increased  $\text{CaCO}_3$  dissolution with depth. Deviations from this trend ("dissolution inversions") are rare and narrowly localized in the Recent ocean — for example, in areas of coastal upwellings, with their exceptionally high bioproductivity, or near acid hydrothermal springs.

The facies changes caused by selective dissolution of  $\text{CaCO}_3$  ultimately create a vertical facies sequence which is universal at least for the pelagic parts of the ocean — a facies sequence of dissolution (Fig. 2) in which the bathymetric position of each facies is defined by the depth of the critical dissolution levels limiting it [16]. Observations in Recent oceans indicate [4, 5, 12] that changes of the critical depth and lysocline levels generally occur in a coordinated fashion, although the amplitude of the shift of each particular level and, therefore, the range of depths occupied by the facies between the levels may vary among climatic zones and facies belts.

The periodic variations of  $\text{CaCO}_3$  contents and the preservation of its biomorphic modifications (the so-called carbonate cycles) observed in the cores of deep-sea sediments and correlating with the stages of Quaternary continental glaciations are due mainly to changed intensities of selective dissolution of biogenic carbonates [21, 44, 46]. In each core the carbonate cycles of dissolution appear as a series of intercorrelated variation curves of dissolution indicators:  $\text{CaCO}_3$  and aragonite contents, the number of pteropod and foraminifer shells, the degree of shell fragmentation, the proportions of planktonic and benthic foraminifers, planktonic foraminifers and radiolarians, and the dissolution indices calculated from



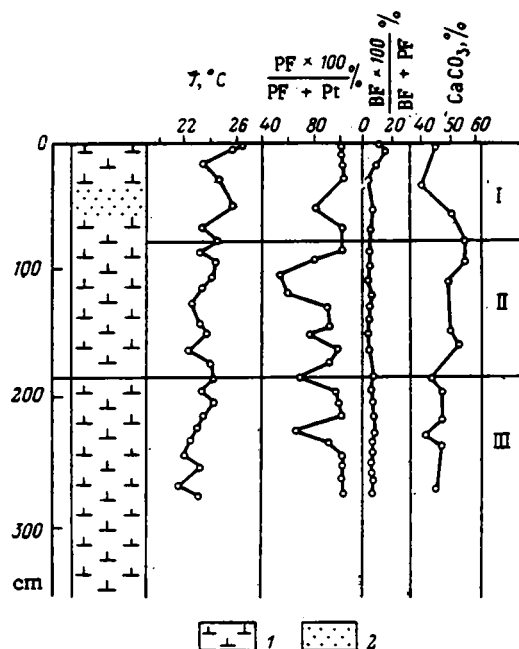


Fig. 3. Variations of facies characteristics of sediments in column II-1 (12°44' N lat, 46°29' E long, depth 1730 m). 1) clay-calcareous ooze; 2) pteropod-foraminiferal sand; T, °C — paleotemperature curve based on planktonic foraminifers. Stratigraphic horizons after [31]: I) Holocene, (II) late glacial stage of the last continental ice age in the Northern Hemisphere (IIa — upper portion; IIb — lower portion); (III) interstadial period; (IV) early glacial stage; (V) interglacial epoch. Other notations as in Fig. 2.

the ratio of more solvable and resistant species [21, 44, 46, 47]. From the values of these dissolution indicators each interval of a profile (corresponding to a climatic-stratigraphic horizon) can be referred to a particular facies in the dissolution series, establishing the position of the critical dissolution levels relative to the depths of the station point. The variations are interpreted as depth shifts of the critical dissolution levels, and a succession of a facies along the vertical in the core indicates the passage of a critical level (lysocline or critical depth) through the station point.

A comparison of the data on the carbonate cycles in the columns from different depths and climate zones shows that Late Quaternary climatic fluctuations were associated with a change of bathymetric position of all levels of  $\text{CaCO}_3$  dissolution and, therefore, of the entire facies series of dissolution. In each region the changes of the individual levels had the same sign during cooling periods (the last ice age stages) and the inverse sign during the warming periods (interglacial epoch, interstadial periods, and the Holocene). It was discovered that in some of the regions, including most of the Atlantic Ocean [20], the entire southern ocean [46, 47], and selected areas of the equatorial Pacific Ocean [40], the facies dissolution series shifted toward shallower depths in the cold epochs (especially during the maximum of the last ice age).

In the Atlantic Ocean, for example, a large number of cores have been collected in the seafloor where the Holocene sediments — carbonate — were deposited above the critical carbonate accumulation depth (CCAD), while the sediments from the last ice age are carbonate-free and reflect the migration of CCAD to lower depths and, as a result, a general reduction of the area of carbonate facies. In many of the cores the poorer preservation of foraminifers indicates a shallower depth of foraminiferal lysocline during the Würm Ice Age. In the Atlantic, the effect of the increased dissolution in the glacial epochs was intensified by the more abundant influx of diluted terrigenous material into the deep-sea basins.

In the Australian sector of the southern ocean, Williams et al. [46] determined that the intensified dissolution in the cold period was compounded by a northward migration of the silica accumulation belt. They discovered a substantial (by 700-800 m) rise of the foraminiferal and carbonate lysoclines on both slopes of the midoceanic ridge during the last ice age accompanied by a reduction of the areas of the high carbonate sediments covering the ridge, which were pushed by diatom ooze to the very crest of the ridge.

In the northern half of the Indian Ocean and in most of the Pacific an inverse picture is observed: a heightened  $\text{CaCO}_3$  content and improved preservation of carbonate shells during glacial epochs as compared with the interglacials [44], reflecting a sinking of the lysoclines and critical depths. Shifts of upper members of the facies dissolution series (relative to shallow water members) can be traced in core II-1 from the northwestern part of the Gulf of Aden, collected at a depth of 1730 m (Fig. 3), which reveals the horizons of Holocene, late glacial stage, and the interstadial period of the last ice age (isotope stages 1-3) [31]. Judging by the good preservation of planktonic foraminifers and the low content of benthic foraminifers, the point remained, throughout this period of time, above the foraminifer lysocline. The structure of planktonic foraminifer thanatocoenosis experienced little change, attesting to stable hydrological conditions [31] in which the preservation of pteropods experienced significant variations. During the Holocene, pteropod shells were virtually absent, while the surface sediment layer has signs of dissolution of the least stable foraminifers, indicating the position of the point near the aragonite lysocline and the level of initial dissolution of foraminifers. The sediments of the late glacial stage of the last ice age contain abundant pteropod shells (see Fig. 3). This may indicate a subsidence of pteropod lysocline and the critical aragonite depth below 1700 m. In the interglacial stage sediments (isotope stage 3), pteropods are rare, probably because of their dissolution at the depths between the lysocline and critical aragonite depth.

In core 28-Pt-7 (depth 3300 m) from the Arabian-Indian ridge in the area of the southern tropical divergence [10], foraminifers are heavily dissolved in the deposits of the last interglacial epoch (isotope stage 5); this indicates the position of the foraminifer lysocline above the core point. The sediments of the last ice age exhibit only weak dissolution features characteristic of the facies above the lysocline, which apparently sunk at that time beneath 3300 m.

In core NO-04-KS6 (depth 3541 m) from the western flank of the East Pacific Rise [44] the dissolution index of foraminifers is drastically increased on the Pleistocene-Holocene boundary, suggesting that lysocline approached a depth of 3.5 km. A similar course of the dissolution index curve is observed in the core IC-5 (depth 4308 m) from the area south of the Bay of Bengal [44]. In the Holocene layer, the dissolution index is high (5.5), indicating that the position of the site is lower than the lysocline. During the glacial stages of the last ice age (isotope stages 2 and 4), the dissolution was expressed weakly and the sampling site was obviously much higher than the lysocline. During the interstadial period and the interglacial epoch (isotope stages 3 and 5) the foraminiferal lysocline, judging by intensified dissolution, approached the depth of the site. Similar CCAD oscillations caused at greater depths the replacement of carbonate-free (silicic-clay or clayey) ooze of the warm epochs by marlstone varieties typical for glaciation periods. The total area of carbonate facies in these regions expanded during cool epochs.

#### INFLUENCE OF GLACIOEUSTATIC FLUCTUATION OF SEA LEVEL ON THE DEEP-SEA FACIES

The eustatic lowering of the level of the world ocean (by 80-150 m during the glaciation maximum, some 180,000 years ago [24, 25]) caused by the last continental ice age in the Northern Hemisphere affected not only the shallow-sea facies but also some of the deep-sea marine and oceanic facies. Everywhere except for some areas in the arid zone [39] the glaciation was accompanied by more intense accumulation of terrigenous turbidites and other types of gravity sediments near the foot of the continental slope in the deep-sea alluvial fans and on subcontinental abyssal plains. The pelagic facies were moved toward the center of the ocean and the weakened terrigenous sedimentation (especially the activity of the turbidity flows during the postglacial eustatic transgression) shifted the pelagic boundary toward the foot of the continental slope.

Deep-sea facies settings were strongly changed by the glacioeustatic lowering of sea level in the basins communicating with the oceans through shallow straits, as is illustrated by the Red Sea, sheltered from the direct influence of continental ice sheets.

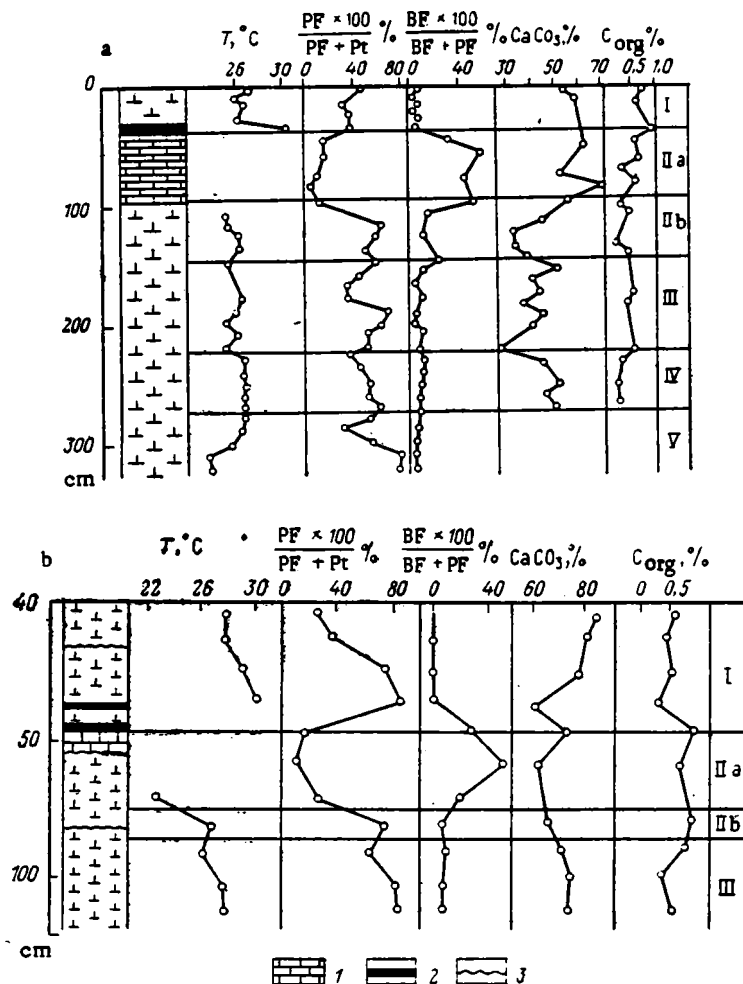


Fig. 4. Variations of facies characteristics of sediments in column III-226 (a) (17°33' N lat, 39°45' E long, depth 686 m) and column II-30 (b) (24°42' N lat, 36°17' E long, depth 1180 m). (1) Clay-calcareous ooze with carbonate crusts; (2) same, enriched in organic matter (sapropel); (3) orange-colored ferruginated interlayers. Other notations and stratigraphic horizons as in Fig. 3.

The Red Sea is connected with the Indian Ocean by the narrow Bab-al-Mandeb strait, with a maximum depth of 136 m. The lithologic and micropaleontologic studies of six cores of deep-sea (686-1350 m) clay-calcareous sediments from central (18°N lat) and northern (25°N lat) parts of the Red Sea [31] have traced in them a similar succession of facies correlating with the main climatic and glacioeustatic events of the Late Quaternary (Fig. 4). A detailed stratigraphy of these profiles, taking into account the oxygen isotope and radiocarbon data is given in [26, 31, 34].

Three lithologic-facies types of carbonate sediments are seen in all the cores, with different structures of planktonic-foraminiferal and pteropod thanatocoenoses. The first type is characteristic of Recent (Holocene) layer (horizon I) and the bottom intervals of all cores corresponding to the early glacial stage (oxygen isotope stage 4, horizon IV), interstadial period (stage 3, horizon III), and the first half of the late glacial stage of the last ice age (horizon IIb). It spans an age range from approximately 72,000 to 20,000 years ago. Lithologically, these are fairly uniform yellowish-gray granulometrically unsorted hemipelagic calcareous and marly coccolith-pteropod-foraminiferal ooze containing from 30 to 85%  $\text{CaCO}_3$  and about 0.4-0.8%  $\text{C}_{\text{org}}$ . The sedimentation rates range from 2.4 to 9.3 cm/1000 years (in the Holocene 3-6 cm/1000 years). Usually, it is faster for the sediments of the early glacial stage and the beginning of the late stage, and slower in the sediments in the interglacial stage and

the Holocene. In the microfauna, planktonic foraminifers (measured by the number of individuals per 1 g of sediment) are usually predominant over pteropods; in some Upper Pleistocene layers pteropod shells are practically absent because of dissolution, indicating a greater aggressiveness of bottom water (a raised level of pteropod lysocline?). In the Upper Pleistocene interval, the content of benthic foraminifers, compared with the total amount, together with planktonic species, (5-20%), is higher than in the Holocene (less than 5%) and much higher than the level typical for normal pelagic coccolith-foraminiferal ooze (2%). This may be attributed to heightened productivity of benthic foraminiferal coenoses. The faunistic complexes of planktonic foraminifers and pteropods varied little throughout the period from the early glacial stage to the latter half of the late glacial stage and differed little from the Recent compositions, indicating a fairly stable hydrologic environment in the Red Sea [31]. The variety of planktonic foraminiferal species in Recent sediments decreases from south to north as one moves away from the Bab-al-Mandeb Strait, i.e., with slackening influence of the Indian Ocean water: at 18°N lat the Holocene sediments contain 25-27 foraminifer species, while at 25°N lat only 16 species are found. In the Lower Pleistocene (horizons IIb-IV) fewer species are found: 22-25 at 18°N lat and 11-17 at 25°N lat, probably indicating a greater isolation of the Red Sea at that time. The numbers of species and subspecies or morphologic forms of pteropods in both areas are approximately the same in the Late Pleistocene and the Holocene (13-15 in each horizon). This is indicative of a lower sensitivity of pteropod fauna (compared with foraminifers) to changed hydrologic conditions (especially a rise of water salinity) with attenuating water exchange with the Indian Ocean.

In the latter half of the late glacial stage — during the maximum of the last ice age (approximately 18,000 years ago) — a drastic change in lithologic and faunistic characteristics of deep-sea facies is observed. Until the latter half of the stage, chemogenic aragonite crusts are formed, which are observed in all the cores studied by us and described by many investigators [29, 38]. The chemogenic precipitation of aragonite and traces of anhydrite crystals [38] are evidence of a high mineral content in bottom or interstitial water and is an indirect sign of hypersalinity of the basin as a whole. The sediments consist of calcareous (CaCO<sub>3</sub> 50-70%) pteropod ooze with rare shells of planktonic foraminifers (hundreds of individuals per 1 g of sediment); the latter's species diversity, however, remains fairly high (20 species at 18°N lat and 11 species at 25°N lat), with only the most stenohaline species being absent. In abundance, pteropods dominate over foraminifers (several thousand individuals per 1 g of sediment), but one eurihaline species is clearly predominant among them: *Gresels* (80-100%). The species diversity of pteropods (11 to 13 species and subspecies) is also rather large. The share of benthic foraminifers (as related to the total) is much greater (up to 60%), because there are less planktonic species. The faunistic data thus confirm the extreme ecological environments, especially the drastic increase in surface water salinity, approaching the tolerance limit of planktonic foraminifers and some of the pteropod species. Calculations with oxygen isotope and paleotemperature data for these cores show that during the glacial maximum the surface salinity rose to some 50 ppt [9]. The raised salinity was caused both by a sharp reduction of exchange with the Indian Ocean, which was the sole source of less salty water influx to the Red Sea that could partly compensate for the intense evaporation, and by the aridization of the climate in this area [8, 31, 41]. The abundance of the real marine pteropod fauna and the large species diversity of pteropods and foraminifers refute the theory proposed by some investigators that the Bab-al-Mandeb Strait had dried out completely; calculations show [38] that it would have resulted in a nearly complete drying of the entire Red Sea. The heightened salinity and the lowering of surface water temperature (by at least 5°C) was due to a greater water density and the resulting more intense vertical mixing of the water column. This could bring to the seafloor water oversaturated in CaCO<sub>3</sub>, from which chemogenic aragonite could precipitate.

Above the interval of pteropod facies with aragonite crusts, a thin (1-5 cm in our cores) layer of dark greenish-gray pteropod-foraminiferal marly ooze occurs, enriched in organic material (the "sapropel facies"), corresponding to the second phase of deglaciation, or the Early Holocene (11,000 to 7000 years ago). The sediments consists mainly of biogenic carbonates (aragonite, calcite, and magnesian calcite) and silt-clayey terrigenous material. CaCO<sub>3</sub> content (not more than 60%) is much lower than in the underlying layer with aragonite crusts. Corg concentration is up to 0.5-0.9% in our cores, although higher values have been recorded elsewhere [38]. The content of authigenic pyrite is rather high, attesting to anaerobic conditions of the early diagenesis.

The abundance of planktonic foraminifers and their contents, as compared with pteropods and benthic foraminifers, rises rapidly at the Pleistocene-Holocene boundary, which agrees

with the relative desalting of surface water (approximately to 43 ppt according to Ivanova's estimates) and the gradual temperature rise. The variety of species of planktonic fauna is also increased substantially. The small proportion (1-5% of the total foraminifers) of benthic foraminifers could be a sign of unfavorable conditions for benthos due to a shortage of oxygen in bottom waters. It is supported by the absence of bioturbation structures.

The appearance of a "sapropel" facies on the floor of the Red Sea at the Pleistocene-Holocene could be attributed to the increased influx of less salty surface water from the Indian Ocean by a eustatic rise of the seafloor level during the course of deglaciation and the increased atmospheric precipitation [41, 43]. The influx of ocean water was conducive to the development of a rich and diverse foraminiferal fauna in the sea. The spread of the light surface layer above the heavy salt deep layer throughout the water body produced a strong stratification of the water column and barred oxygen-rich surface water from reaching the seafloor. This produced stagnation of bottom water and the development of a "sapropel" facies, as well as increasing biological productivity.

This paleoceanographic situation was apparently unstable. By the middle of the Holocene, a stable circulation of Red Sea waters was established, similar to that observed currently, which halted the accumulation of "sapropel" sediments.

\* \* \*

During the Late Quaternary all the main types of deep-sea sedimentation settings existed in the world ocean, with facies exhibiting all the lithologic and micropaleontologic characteristics observed also in the Recent epoch. Like today, these facies were organized into systems of latitudinal, circumcontinental, and vertical zonality. The response of the deep-sea facies systems to changes caused by the spread or thawing of ice sheets of the last continental ice age in the Northern Hemisphere involved lateral and vertical shifts of the facies: (a) the latitudinal facies zones (except for the equatorial zone), with their characteristic micropaleontological complexes, were shifted toward the equator in the cold epochs (the glacial stages) and toward the poles in the warm epochs (interglacial epoch, interstadial periods, and the Holocene), which was a reflection of the displacement of surface water masses and the hydrological fronts separating them; (b) the facies series of selective dissolution of  $\text{CaCO}_3$  and the individual critical dissolution levels (lysoclines and critical depths) were shifted in the cold epochs compared with the warm periods relative to the bathymetric profile; the direction of this shift was not the same in different regions; the shifts of the dissolution series, which reflected the changed dissolution settings in bottom water, must have been associated with the variations of volumes, physicochemical properties, and intensities of bottom water flows from polar regions and partly with altered bioproductivity of waters; and (c) near-continental facies of terrigenous sediments were shifted seaward in glacial epochs, pushing the pelagic facies further into the sea.

With special reference to the Red Sea, we have shown that in semiclosed basins communicating with the ocean through shallow straits the principal factor of the drastic change of deep-sea facies was the altered intensity of water exchange with the ocean which experienced glacioeustatic fluctuations of its level. A profound change of deep-sea facies in the Red Sea was produced wholly by the glacioeustatic lowering of the ocean level during the last glacial maximum, when the water exchange with the Indian Ocean was at its minimum. The transition from the setting of a hypersaline basin of the late glacial stage with an extremely limited water exchange to the Recent state of the Red Sea was marked by a short-lived blooming of planktonic fauna in surface waters and stagnation of bottom waters. The transient stage in the accumulation of sapropel interlayers, encompassing the deglaciation period, can probably be associated with the unstable hydrologic conditions and the ecological system of the sea. If that is so, the stagnation would stop after steady state set in, with the ocean rising to a higher level in the postglacial times.

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DISTRIBUTION OF ARSENIC IN SUSPENDED AND BOTTOM SEDIMENTS  
IN FRESH-WATER BODIES

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UDC 550.4:551.312

The distribution of total arsenic and several arsenic compounds in suspended and bottom sediments in surface waters of mountainous regions was studied. The grain size of the suspension, the pH, and the mineralization of the water determine the phase and spatial distribution of arsenic in the water bodies.

Natural arsenic compounds are only slightly soluble and are readily adsorbed by mineral sorbents. Therefore a significant proportion of the arsenic is transported in rivers as suspended material. Compared to soluble forms, the arsenic content in suspended and bottom sediments in surface waters has been poorly studied. Substantial gaps in available information make it very difficult to resolve a number of questions on the geochemistry of arsenic.

According to the literature, the arsenic content in suspended and bottom sediments in fresh-water bodies varies widely (0.5-306 mg/kg), in exceptional cases reaching 5 g/kg [6], but averages 5-22.1 mg/kg [4, 6, 7, 9, 11, 12]. If the average arsenic content in soil and rock is taken as 1.4-5 mg/kg [1, 2], the enrichment of bottom sediments in arsenic is apparent.

Questions as to the type of compound and the phase and spatial distribution of arsenic in suspension in fresh-water bodies have essentially not been examined in the literature. Of special interest in the present study are surface waters in mountainous regions, which are characterized by increased turbidity and sharp changes in hydrologic conditions depending on river current. We have chosen to study rivers, lakes, and reservoirs in Soviet Georgia, Armenia, and adjacent regions. Field data were collected mainly in 1975-1984. For the purpose of evaluating the effects of the activities of man, the arsenic content of suspended and bottom sediments of the Debeda and Lukhuni rivers, in the drainage basin of which arsenic polymetallic and sulfide ores are mined and processed, was also studied.

The As content in samples of water, suspension, and sediments was determined according to methods described in [3, 13].

Questions of regional and seasonal distribution of  $As_{sol}$  in Georgia were examined in [4]. According to data obtained in 1980-1984, the  $As_{sol}$  content in uncontaminated surface waters in Georgia and Armenia ranges from less than 0.1 to 16.5  $\mu\text{g/liter}$ . It increases with a decrease in turbidity of river water and a decrease in the elevation of the river basin (Tables 1-3).

Arsenic in Suspension and Bottom Sediments in Surface Waters. The arsenic content in suspension ( $As_{sus}$ ) in rivers of Soviet Georgia ranges from 0.1 to 46.3  $\mu\text{g/liter}$ , which amounts to 4-96% of  $As_{tot}$  (see Table 1). Arsenic in suspension averages 77% of  $As_{tot}$ .

The regional and seasonal distribution of  $As_{sus}$  is determined by the turbidity of the water. An increase in turbidity is accompanied by an increase in both the amount and proportion of arsenic in suspension (see Table 2). The maximum  $As_{sus}$  content is found in summer in rivers in high, mountainous regions (see Table 3). The proportion of arsenic in suspension also increases with an increase in the elevation of the river basin. The  $As_{sus}$  content amounts to 44-55% of  $As_{tot}$  in lowland regions, while in upland and mountainous rivers it is 84-96% (see Table 1).

The arsenic content in suspension in river water ranges over a wide interval (see Tables 1 and 4). It decreases with an increase in turbidity and elevation of the river basin

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Tiflis State University. Translated from *Litologiya i Poleznye Iskopaemye*, No. 1, pp. 17-23, January-February, 1987. Original article submitted March 26, 1985.

TABLE 1. Content of Arsenic in Solution and Suspension in Soviet Georgia

| River, sample location    | Number of samples | pH   | $\Sigma_i$ | Turbidity | $As_{sol}$    |       | $As_{sus}$    |                  | $As_{sus}^*$ % of $As_{tot}$ |
|---------------------------|-------------------|------|------------|-----------|---------------|-------|---------------|------------------|------------------------------|
|                           |                   |      | mg/liter   | mg/liter  | $\mu g/liter$ | mg/kg | $\mu g/liter$ | mg/kg suspension |                              |
| Kura (AkhaIdaba)          | 3                 | 7.85 | 215        | 143       | 3.6           | 16.7  | 4.1           | 28.7             | 53.2                         |
| Kura (Mtskheta)           | 6                 | 7.84 | 335        | 451       | 2.5           | 7.5   | 7.0           | 15.5             | 79.7                         |
| Kura (below Rustavi)      | 6                 | 7.54 | 440        | 136       | 4.1           | 9.3   | 3.2           | 23.5             | 43.8                         |
| Aragvi (mouth)            | 5                 | 7.90 | 405        | 437       | 2.3           | 7.5   | 5.8           | 13.2             | 71.6                         |
| Liakhvi (mouth)           | 2                 | 8.25 | 200        | 469       | 1.7           | 8.5   | 4.5           | 3.6              | 72.6                         |
| Alazani (Chiaura)         | 2                 | 7.59 | 433        | 517       | 2.8           | 6.5   | 5.8           | 11.2             | 67.4                         |
| Rioni (Oni)               | 4                 | 7.74 | 172        | 1876      | 1.2           | 7.0   | 27.8          | 14.8             | 95.0                         |
| Rioni (Ambrolauri)        | 4                 | 7.90 | 169        | 958       | 3.2           | 18.9  | 38.5          | 40.2             | 92.3                         |
| Rioni (Zhoneti)           | 7                 | 7.95 | 216        | 376       | 2.2           | 10.2  | 8.7           | 23.1             | 79.8                         |
| Rioni (Sakochakidze)      | 2                 | 7.65 | 200        | 168       | 2.0           | 10.0  | 2.4           | 14.2             | 54.5                         |
| Ritsula (mouth)           | 2                 | 7.15 | 90         | 200       | 0.9           | 10.0  | 2.2           | 11.0             | 71.0                         |
| Tskh. Tskali (Lentekhi)   | 2                 | 7.82 | 177        | 577       | 1.7           | 9.6   | 8.7           | 15.1             | 83.7                         |
| Tskh. Tskali (mouth)      | 2                 | 7.81 | 200        | 761       | 2.0           | 10.0  | 10.9          | 14.3             | 84.5                         |
| Kvirila (mouth)           | 3                 | 7.60 | 281        | 969       | 0.7           | 2.7   | 5.1           | 5.3              | 87.9                         |
| Vzzyb' (mouth)            | 2                 | 7.74 | 141        | 123       | 2.3           | 16.3  | 2.3           | 18.7             | 50.0                         |
| Galidzga (mouth)          | 2                 | 7.81 | 241        | 2720      | 2.7           | 11.2  | 31.4          | 11.4             | 92.1                         |
| Inguri (Ipri)             | 2                 | 7.88 | 121        | 293       | 1.2           | 9.9   | 4.1           | 14.0             | 77.4                         |
| Ingud (mouth)             | 2                 | 7.72 | 151        | 412       | 0.6           | 4.0   | 6.9           | 16.7             | 92.0                         |
| Chorokhi (mouth)          | 2                 | 8.05 | 137        | 1304      | 2.1           | 15.3  | 26.1          | 20.0             | 92.6                         |
| Terek and its tributaries | 6                 | 7.91 | 182        | 2543      | 0.8           | 4.4   | 15.2          | 6.0              | 95.0                         |
| Glacial streams           | 7                 | 7.41 | 92         | 1212      | 1.0           | 10.9  | 6.8           | 5.6              | 87.2                         |

\*Proportion of dissolved arsenic in water solids.

TABLE 2. Relationship between  $As_{sol}$  and  $As_{sus}$  Content and Turbidity of River Water (ten samples in each group)

| Turbidity, mg/liter | $\Sigma_i$ | $As_{sol}$ | $As_{sus}$    |                 | $As_{sus}^*$ % of $As_{tot}$ |
|---------------------|------------|------------|---------------|-----------------|------------------------------|
|                     | mg/liter   |            | $\mu g/liter$ | mg/g suspension |                              |
| 3-79 (32)*          | 272        | 2.9        | 1.2           | 37.5            | 29.3                         |
| 94-123 (107)        | 264        | 2.6        | 4.1           | 38.3            | 61.2                         |
| 124-251 (184)       | 210        | 2.3        | 2.7           | 14.7            | 54.0                         |
| 274-415 (340)       | 168        | 1.5        | 5.6           | 16.5            | 78.9                         |
| 446-859 (647)       | 145        | 1.2        | 7.6           | 11.7            | 86.4                         |
| 860-1780 (1134)     | 235        | 2.5        | 15.9          | 14.0            | 86.4                         |
| 2000-6100 (3250)    | 191        | 1.0        | 23.3          | 7.2             | 95.9                         |

\*Average value in parentheses.

(see Tables 2 and 3) and increases with an increase in the man-made load (Kura River below Rustavi, the Rioni at Ambrolauri and Zhoneti, etc.; see Table 1). The minimal turbidity of river water during autumn and winter determines the maximum arsenic content in suspension.

Except for those rivers contaminated by industrial arsenic (the Lukhuni, Debeda, and middle course of the Rioni), the arsenic content in bottom sediments is less than that in suspended material (see Table 4). Downstream, and with a decrease in the average elevation of the basin, the arsenic content in bottom sediments increases. In addition to sedimentary sorting of suspended material, the activities of man play a major role in this distribution. The greatest arsenic content was found in bottom deposits of the Lukhuni and Debeda rivers and below their mouths in the Kura and Rioni rivers. Both rivers transport a considerable amount of industrial arsenic. The pattern of accumulation of As in the upper layers of bottom sediment can be explained by man-made activities, which increase through time. However, one should not exclude the possibility of the redistribution of arsenic into lower layers of sediment during diagenesis.

Forms of Arsenic in Suspended and Bottom Sediments of Surface Waters. Despite the usual convention, the study of forms of arsenic in suspended and bottom sediments of surface waters was carried out by a method worked out for polymetallic ores with a low arsenic content [5]. In this method the oxide, sulfide, and silicate forms of arsenic in the sample are sequential-

TABLE 3. Relationship between  $As_{sol}$  and  $As_{sus}$  Content and Average Elevation of River Basin

| Elevation, km | No. of samples | $\Sigma i$ | Turbidity | $As_{sol}$    | $As_{sus}$    |                  | $As_{sus} \cdot \%$ of $As_{tot}$ |
|---------------|----------------|------------|-----------|---------------|---------------|------------------|-----------------------------------|
|               |                | mg/liter   |           | $\mu g/liter$ | $\mu g/liter$ | mg/kg suspension |                                   |
| Up to 1       | 4              | 483        | 259       | 5,0           | 3,9           | 31,4             | 43,8                              |
| From 1 to 1,5 | 11             | 317        | 301       | 2,5           | 4,9           | 20,9             | 66,2                              |
| From 1,5 to 2 | 21             | 197        | 544       | 1,7           | 9,3           | 21,5             | 84,5                              |
| From 2 to 2,5 | 11             | 179        | 665       | 2,7           | 7,6           | 22,5             | 73,8                              |
| From 2,5 to 3 | 8              | 120        | 1325      | 0,9           | 9,3           | 11,2             | 91,2                              |
| >3            | 5              | 156        | 2420      | 0,6           | 12,2          | 9,5              | 95,3                              |

TABLE 4. Distribution of Arsenic in Suspended and Bottom Sediments

| Body of water                       | Sample     | No. of samples | As, mg/kg*      |
|-------------------------------------|------------|----------------|-----------------|
| Rivers of Georgia                   | Suspension | 66             | 2.6—66,7 (15,4) |
| Rioni River (middle course)         | "          | 11             | 12—140 (45,4)   |
| Lukhuni River                       | "          | 23             | 40—1310 (90,9)  |
| Rivers of Georgia                   | Sediment   | 23             | 6—28 (13,7)     |
| Black Sea (mouth of Chorokhi River) | "          | 8              | 5—21,5 (11,8)   |
| Lakes of Georgia                    | "          | 6              | 1,3—15,6 (6,1)  |
| Sevan Lake                          | "          | 15             | 2,5—20,5 (12)   |
| Lukhuni River                       | "          | 11             | 123—1030 (507)  |

\*Both range of content and average (in parentheses) are given.

ly bathed in a 2 N solution of HCl, a 4 N solution of NaOH, and a mixture of  $HNO_3$  and  $H_2SO_4$ . In addition, the composition of acid extracts of various concentrations taken from bottom sediments was studied. The acid-soluble arsenic was recalculated to provide the solid phase, the soluble portion, and the proportion of total arsenic ( $As'HCl$ ,  $As''HCl$ , and  $As_{HCl}$ , respectively).

The distribution of the forms of arsenic in suspended and bottom sediments is markedly affected by changes in the average elevation of the river basin (Fig. 1). With an increase in the solid phase, the proportion of the silicate form of arsenic increases and the sulfide and oxide forms (including adsorbed) decrease. This distribution of the forms is explained by variations in the grain size and mineralogical composition of the solid phase along the course of the river.

On the basis of the possible formation of arsenic oxides from sulfides, they may have a different distribution along the river course. Oxidation of sulfides in the river is commonly compensated by the formation of organic forms of arsenic. It is not possible to determine the latter by the analytic methods we used.

With an increase in concentration of HCl to 1 N the amounts of  $As_{HCl}$  and  $As'HCl$  increased appreciably. Further increase in the concentration of the acid had little effect. Bottom sediments of lowland waters exceed those of high mountain rivers in their content of  $As_{HCl}$ , and especially  $As'HCl$ . This distinction is particularly sharply expressed at low concentrations (0.01-0.1 N) of the acid extracts, which indicates that sediments of lowland waters are enriched in mobile forms of arsenic (ion-salt, adsorbed, carbonate-connected, etc.). It is typical that the  $As_{HCl}$  content in sediments of lowlands and mountains differ little at concentrations of HCl greater than 0.5 N.

The distribution of  $As''HCl$  is singular. The  $As''HCl$  content in acid extracts of bottom sediments from lowland waters, in contrast to the  $As_{HCl}$  and  $As'HCl$  content, has a small maximum at low acid concentrations. Dilute HCl washes out the mobile forms of arsenic, affecting the silicate form of the solid phase less than indicated in the maximum.

Role of Adsorption Processes in Arsenic Distribution in Surface Waters. Arsenites and arsenates are readily adsorbed by clay minerals, heavy-metal hydroxides, and other natural

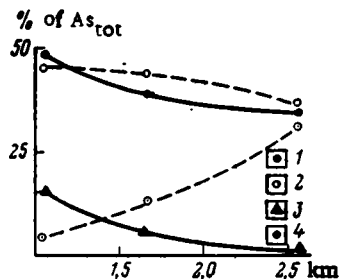


Fig. 1

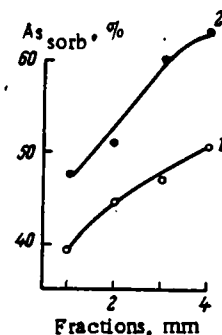


Fig. 2

Fig. 1. Relationship between content of oxide (1), sulfide (2), adsorbed (3), and silicate (4) forms of arsenic in suspended and bottom sediments in rivers and the elevation of the basin.

Fig. 2. Relationship of the amount of adsorbed arsenic to the grain size of bottom sediments (1) and suspended sediments (2) in the Kura River (average diameter of grains reported in Table 6).

TABLE 5. Relationship of Arsenate Adsorption on Natural Sorbents to the Sorbent-Sorbitive Ratio, %

| Sorbent-sorb-<br>tive ratio,<br>mass | Fe(OH) <sub>3</sub> |                      | CaCO <sub>3</sub> | Suspension     |               | Bottom sediment |               |
|--------------------------------------|---------------------|----------------------|-------------------|----------------|---------------|-----------------|---------------|
|                                      | air-dried           | newly de-<br>posited |                   | Terek<br>River | Kura<br>River | Terek<br>River  | Kura<br>River |
| 0,0005                               | 60                  | 71                   | 36                | 15             | 28            | 13              | 24            |
| 0,0015                               | 70                  | 80                   | 50                | 28             | 34            | 25              | 32            |
| 0,0025                               | 80                  | 80                   | 66                | 48             | 55            | 42              | 48            |
| 0,0050                               | 85                  | 90                   | 68                | 55             | 64            | 51              | 60            |
| 0,0100                               | 87                  | 91                   | 70                | 62             | 70            | 58              | 63            |
| 0,0150                               | 90                  | 92                   | 74                | 64             | 74            | 62              | 66            |
| 0,0400                               | 90                  | 92                   | 78                | 70             | 76            | 68              | 70            |

sorbents [1, 8, 10]. Thus surface processes should play a paramount role in interphase redistribution of arsenic in rivers.

In model studies of suspensions in river waters, bottom sediments, calcium carbonate, and iron (III) hydroxide, the effect of various factors on the adsorption distribution of arsenates was sought. Depending on the nature of the sorbent, phase equilibrium was essentially attained within a 12-24-h period and the ratio of sorbent to sorbitive was determined (Table 5). By the time that the sorbent exceeds the sorbitive by 2500-5000 times, more than 50% of the dissolved arsenic has entered the solid phase. Conditions for the adsorption of arsenic are more favorable in upland waters, since the turbidity reaches  $n \cdot 100$  mg/liter while the  $As_{sol}$  is  $n$   $\mu$ g/liter.

The adsorption capacity of sorbents is known to depend on many factors, including grain size. The fine fractions ( $d < 0.003$  mm) of suspended and bottom sediment adsorb 12-15% more arsenic than the coarse fractions ( $d > 0.03$  mm) (Fig. 2). The greater activity of finely dispersed sorbent is due to not only the increase in specific surface area but also an increase in clay minerals and metallic hydroxides that accompanies greater dispersion of suspended and bottom sediments.

The most important factor in the redistribution of arsenic phases is the pH of the liquid phase [10]. The maximum adsorption of arsenates by natural sorbents is found to be in the area of pH 7-8, which is typical for most natural waters (Fig. 3). The optimum value of the pH depends on the type of sorbent and is probably determined by the specific arsenic compound (in setting up the model, samples of suspended and bottom sediments were first converted to the  $H^+$  form by acid treatment).

The results obtained provide explanation for certain aspects of arsenic distribution in surface waters. In particular, changes in the grain size distribution of suspended and bottom



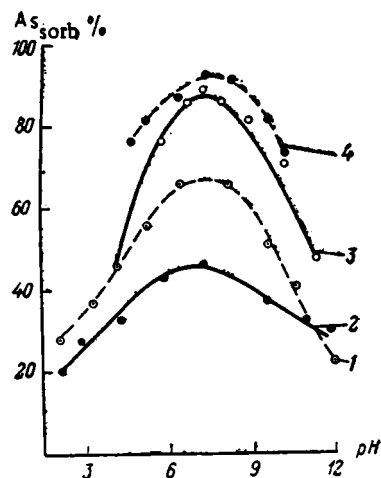


Fig. 3.

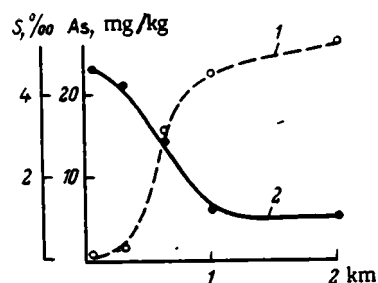


Fig. 4

Fig. 3. Relationship between amount of adsorbed arsenic and pH of the solution. 1) Bottom deposits of the Kura River in  $H^+$  form; 2) bottom deposits of the Terek River in  $H^+$  form; 3) air-dried  $Fe(OH)_3$ ; 4) newly deposited  $Fe(OH)_3$ .

Fig. 4. Relationship between salinity of seawater (1) and arsenic content in bottom sediments (2) and distance from the mouth of the Chorokhi River.

TABLE 6. Relationship of Arsenic Content in Suspended and Bottom Sediments to Grain Size, mg/kg

| River                               | No. of samples | Av. diam. of grains, mm |       |       |       |
|-------------------------------------|----------------|-------------------------|-------|-------|-------|
|                                     |                | 0,03                    | 0,015 | 0,008 | 0,003 |
| Uncontaminated rivers               | 4              | 12,5                    | 14,1  | 13,7  | 16,9  |
| Rivers from mining districts        | 3              | 11,9                    | 9,9   | 13,5  | 14,9  |
| Lukhuni River (bottom sediments)    | 2              | 301                     | 689   | 422   | 193   |
| Lukhuni River (suspended sediments) | 2              | 74                      | 60    | 62    | 68    |

TABLE 7. Effect of Mineralization of the Water on Adsorption and Desorption of Arsenates

| Medium           | Mineralization, g/liter | Adsorption, % |                     | Desorption, % of $As_{sorb}$ |                     |                   |
|------------------|-------------------------|---------------|---------------------|------------------------------|---------------------|-------------------|
|                  |                         | $Fe(OH)_3$    | Kura River sediment | $Fe(OH)_3$                   | Kura River sediment | oceanic sediments |
| Distilled water  | 0,005                   | 90            | 44                  | 0                            | 2                   | 2                 |
| Kura River water | 0,36                    | 88            | 44                  | 1                            | 8                   | 3                 |
| Black Sea water  | 17,2                    | 80            | 37                  | 8                            | 18                  | 4                 |
| Oceanic water    | 35,5                    | 78            | 28                  | 13                           | 38                  | 6                 |

sediments along the course of rivers (or a decrease in the average elevation of the river basin) are associated with an increase in the sorption capacity, and consequently an increase in the content of the adsorbed form of arsenic (see Fig. 1). The relationship between adsorbed arsenic and the sorbent-sorbitive ratio is reflected in the presence of an inverse relationship between turbidity of river water and the content of arsenic in suspension (see Tables 2 and 5). Predominance of the coarse fraction in bottom deposits compared to suspension decreases the adsorption capacity and accordingly the arsenic content (see Table 4).

Natural processes are complex, and it is difficult to model them accurately. Moreover, changes in one hydrochemical parameter or another can be caused by a large number of factors.

For example, an increase in the arsenic content with greater dispersion of the solid phase (Table 6) cannot be explained by increased adsorption activity alone. As a result of variations in grain size, the arsenic content in the fine fraction increases an average of 30%, while in analogous circumstances the adsorption capacity of suspended and bottom sediments increases 12-15% (see Fig. 2). The remainder of the increase in arsenic is the result of mineralogical sorting in the fine fractions and the accumulation of a relatively enriched clay fraction. A different distribution of arsenic through the grain size spectrum of the solid phase is found in rivers in mining districts or where there is contamination by industrial arsenic (see Table 6). The tendency toward accumulation of arsenic in the coarse (heavy) fraction is due to the high density (3.4-6.2) of arsenic sulfide minerals. Phase analysis has shown that an average of 41% and 71% of  $As_{tot}$  in Lukhuni River sediments is in sulfide form.

The patterns shown in suspension models (Tables 5-7) are not always found in nature because of the narrow range of variation of hydrochemical parameters. Thus, the increase in arsenic content in suspended sediments in the pH range optimal for adsorption is weakly expressed. Contrary to expectations, with an increase in the total ions ( $\Sigma_1$ ) in river water the arsenic content in suspended sediments does not decrease, but increases (see Table 3). The inconsistency between laboratory results and natural observations has a formal basis. The fact is that with an increase in  $\Sigma_1$  in river water, as a rule the content of  $As_{sol}$  and the degree of dispersion of suspended material increase and the turbidity decreases (usually  $\Sigma_1$  increases in the lower course of the river). These trends promote the enrichment of suspended material in arsenic, and the inverse relationship between  $\Sigma_1$  and  $As_{sus}$  is obscured.

When there is a sharp increase in the mineralization of the water, laboratory results and natural observations coincide. Thus, away from the mouth of the Chorokhi River into the depths of the Black Sea, an increase in salinity is accompanied by a decrease in the arsenic content of the bottom sediments (Fig. 4). It would be difficult to explain this distribution of arsenic without considering surface processes, since the arsenic content of bottom sediments should increase away from the river mouth as a result of sedimentary sorting and increased dispersal.

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GENETIC TYPES OF CARBONATES OF LATE QUATERNARY SEDIMENTS  
OF THE BLACK SEA

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UDC 552.54(262.5)

The paper analyzes the genetic types of carbonates of Quaternary sediments of the Black Sea. Their role in the formation of total carbonate content of the sediments is examined and the problems of their evolution are discussed.

Late Quaternary sediments of the Black Sea contain a large amount of carbonates derived from different sources. The mode of occurrence of carbonates in the sediments of individual regions, facies zones, and different-age horizons has been repeatedly examined by Soviet and foreign authors [1-8]. However, specific problems in the analysis of genetic types of carbonates of Black Sea sediments, their interrelations, role in the formation of total carbonate content, and evolution throughout the late Quaternary when sedimentation conditions changed markedly have not been treated in the scientific literature, although recent mass utilization of x-ray methods and electron microscopy has led to a more precise identification of different types of carbonates in sediments.

To solve these problems we studied more than 300 sediment cores of recent Black Sea deposits (from the present to 3000 years B.P.), Old Black Sea beds (3000-8000 years B.P.), and Neoeuxinian sediments (8000-20,000 years B.P.) of the shelf, continental slope, and adjacent parts of the basin in the western, northern, and eastern parts of the Black Sea. Samples from 110 cores were examined by x-ray methods to study the mineral composition of the carbonates; in 20 sediment cores studies were made of the total sample. A total of more than 250 diffractograms was obtained. The morphology of the carbonate particles was studied using a polarizing and a binocular microscope. Samples from 20 cores (total sediment samples as well as some fractions) were examined using the high-resolution scanning electron microscope "Quickscan-106."

Late Quaternary sediments of the Black Sea have a variable carbonate content both areally and in cross section (Fig. 1). Beyond the littoral zone maximum concentrations of  $\text{CaCO}_3$  have been observed in coquinas (shell limestones) of the northwestern and Kerch'-Taman' areas of the shelf, where they comprise 50-90% of the material. In other areas of the shelf the carbonate content ranges between 10 and 30%. In contemporary muds of the deep-sea basin two fields with high (50-60%) carbonate concentrations have been recorded in the western and eastern halistatic (oxygen-deficient) zones of the sea. In areas of the basin adjacent to mountainous shores of the Crimea, Caucasus, and Turkey the carbonate content rises abruptly above 20%. Old Black Sea beds of the basin have about the same carbonate content.

The carbonate content in Neoeuxinian sediments of the shelf is lower than that in overlying deposits, with the fields of occurrence of coquinas decreasing. Beyond the shelf in the western half of the basin carbonate content in the upper part of Neoeuxinian muds increases to 50-80%. Downward in the sediment section the carbonate concentrations decrease abruptly and in typical cinnamon-brown muds of the glacial maximum (15,000-18,000 years B.P.) do not exceed 10-15%. Mud of the eastern half of the basin have a low carbonate content.

On the basis of our determinations, biogenous, terrigenous, and chemogenic varieties of carbonates were identified in the sediments examined.

Biogenous carbonates are represented in the sediments mainly by bivalve molluscs, gastropods, benthonic foraminifera, ostracods, coccolithophorids and calcareous algae. A large part of the entire shells and shelly detritus is concentrated in the  $>0.1$ -mm fractions.

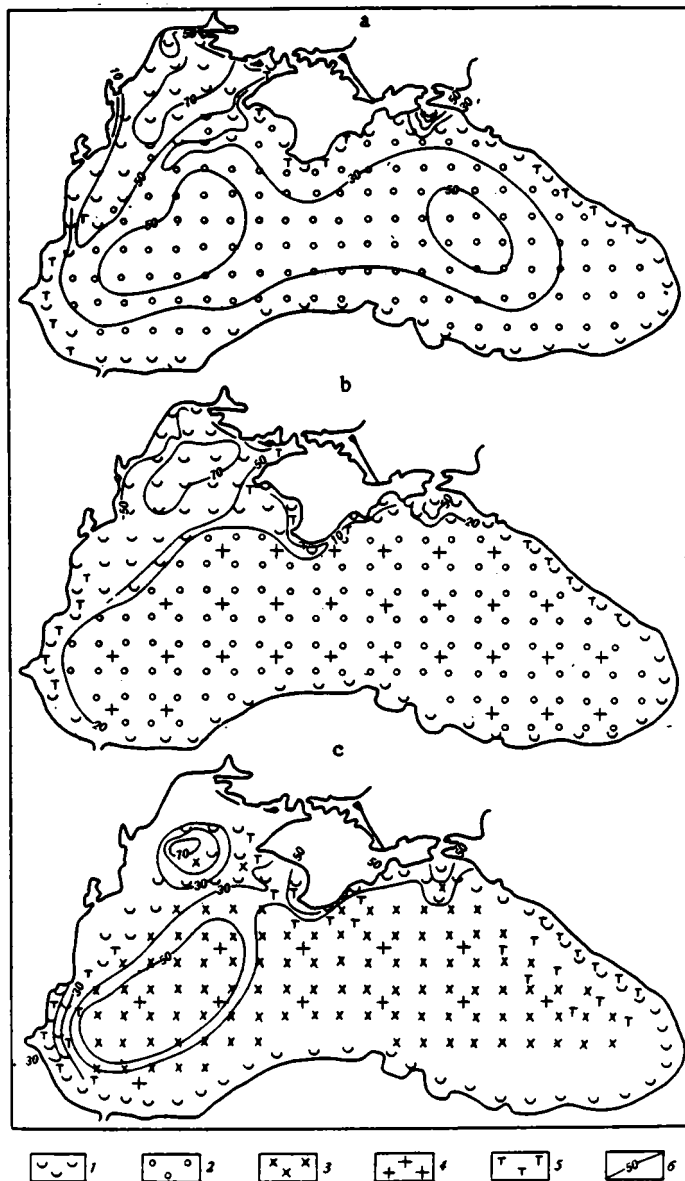


Fig. 1. Occurrence of genetic types of carbonates (a — in recent deposits, b — in Old Black Sea beds, c — in late Neoeuxinian sediments). 1) Biogenous skeletal carbonates; 2) biogenous coccolithic carbonates; 3) chemogenic sedimentary carbonates; 4) diagenetic carbonates; 5) terrigenous carbonates; 6) lines of equal carbonate concentrations, %.

Among the silt-size particles are finely divided shelly detritus, juvenile valves, minute foraminifera, and ostracods. The bulk of the coccolithophorids is contained in the <0.005-mm fractions.

Biogenous carbonates are in a quantitative sense the most common type of carbonates in late Quaternary sediments. They are predominant in modern and ancient Black Sea deposits and often become the principal sediment-forming component. In the northwestern and Kerch'-Taman' areas of the shelf they compose large fields of coquinas. Beyond the area of occurrence of coquinas in predominantly terrigenous shelf deposits biogenous carbonates continue to be the most common type, although their relative importance among the other carbonates decreases.

The bulk of biogenous carbonate material on the shelf is incorporated into sediments by bivalve molluscs. Remains of benthonic foraminifera and ostracods play a secondary role (Fig. 2a). Calcareous algae in some areas of the shelf (for example, Karkinit Bay) are of

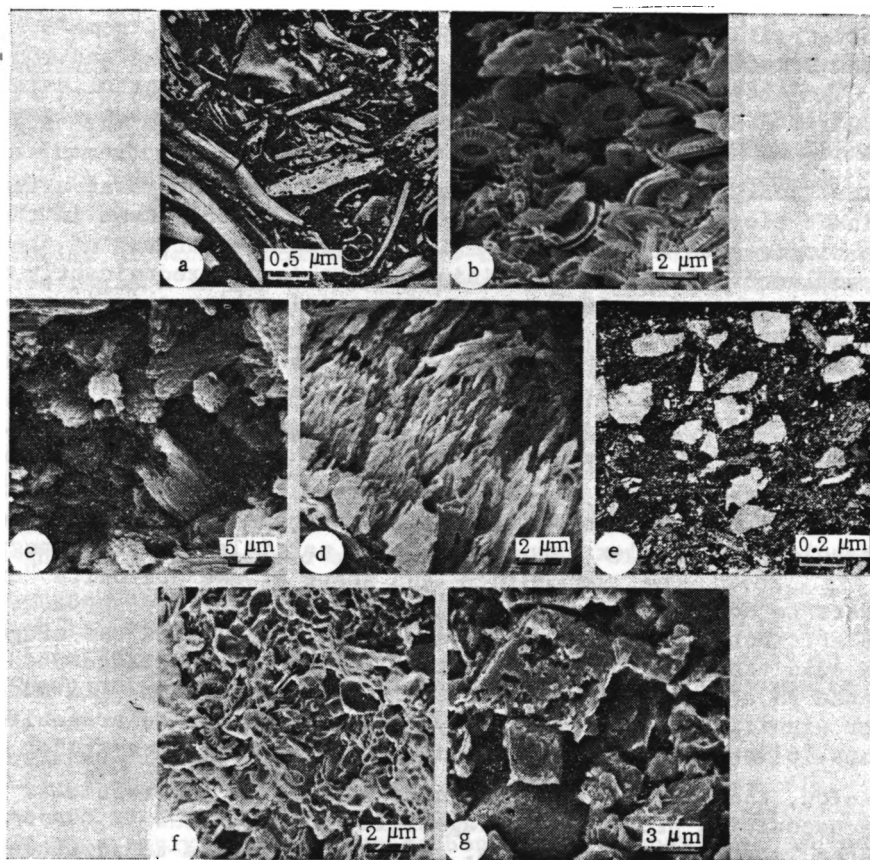


Fig. 2. Photomicrographs of carbonates: a) remains of molluscan shells and benthonic foraminifera (thin section, crossed nicols, scale 0.5 mm); b) coccoliths (SEM, scale 2  $\mu$ m); c) aragonitic grains (SEM, scale 5  $\mu$ m); d) aragonitic shell fragment (SEM, scale 2  $\mu$ m); e) calcareous rock fragments (thin section crossed nicols, scale 0.2 mm); f) diagenetic carbonate crystals (SEM, scale 2  $\mu$ m); g) sedimentary calcite crystals (SEM, scale 3  $\mu$ m).

relatively great importance among the biogenous carbonates. Molluscan shells and rock fragments are commonly overgrown with them in shallow water, forming large (up to 3 cm in diameter) round "concretions." Coccoliths in the form of a small admixture are almost always present in shelf sediments. In individual areas of the outer shelf their importance among the biogenous carbonates increases and they become the principal component of fine-grained carbonate-rich muds.

Beyond the shelf coccolithophorids play a major role among the biogenous carbonates. In sediments of the western and eastern parts of the deep-sea basin they are the principal component of contemporary muds in which they compose numerous thin (<2 mm) laminae consisting entirely of the coccolithophore *Emiliana huxleyi* (see Fig. 2b). In Old Black Sea sapropelic muds the number of coccoliths decreases sharply, and they form only individual layers.

In Neoeuxinian deposits the role of biogenous carbonates decreases. On the shelf of the northwestern and Kerch'-Taman' regions the coquinas occupied much smaller areas than today (see Fig. 1). The older sediments, which had been deposited during the glacial maximum, contain minimum amounts of biogenous carbonates represented by molluscan shells. In other areas of the shelf the importance of molluscan shells is comparable to that of other types of carbonates. In deep-sea basin deposits, except for the upper zone of the continental slope where shell fragments are rare, biogenous carbonates hardly accumulated at all in Neoeuxinian time.

X-ray diffraction studies of sediment-forming shells have shown that most Black Sea pelecypods (*Dreissena*, *Monodonta*, *Cardium*, *Spisula*, *Pitar*, *Abra*, *Chione*, *Paphia* et al.) and gas-

tropods construct their skeletons from aragonite. The shells of some molluscan species (*Ostrea Balanus*) and coccoliths have a calcite composition. *Mytilus* and *Modiolus* have a mixed type of shell. The outer prismatic layer of the mussels consists of calcite and the inner layer consists of aragonite. Benthonic foraminifera and calcareous algae are composed of magnesite (up to 9%  $\text{MgCO}_3$ ).

Mineralogical analysis of total sediment samples has shown that aragonite and calcite are the predominant biogenous carbonates. Aragonite is predominant in those areas of the shelf where the biocoenoses are composed mainly of representatives of the above-mentioned characteristic molluscs. In post-Neoeuxinian time this is predominantly the shallow-water zone of the sea to depths of ~30 m, and in Neoeuxinian time this is practically the entire shelf. Calcite is most common in the zone of modern and ancient mytilid and *Phaseolina* muds where, together with aragonite, it composes the shells *Mytilus* and *Modiolus*. In Neoeuxinian shelf sediments no biogenic calcite was observed in large amounts.

Biogenic calcite is the predominant mineral in post-Neoeuxinian deep-sea deposits inasmuch as coccoliths are composed of them. Only in the lowermost strata of Old Black Sea sapropel is aragonite detected in some calcareous layers. In microscopic studies these aragonite formations show no evidence of a biogenic habit. Aragonite particles have a needlelike and rice-shaped morphology, a complex structure, and a particle diameter ranging from 2 to 10  $\mu\text{m}$  in size (see Fig. 2c). The composition and shape of the aragonite "crystals" have enabled some investigators to consider them as abiogenic formations [8]. However, whenever a chemogenic origin is attributed to aragonite layers it is unclear how the aragonite was precipitated from less cold than present (+9°C) waters, obviously undersaturated at depth with respect to carbonate as a result of hydrogen sulfide contamination. In addition, the aragonite particles differ significantly in morphology from the chemogenic aragonite monocrystals of Red Sea sediments [6] and are most likely bioaggregates of monocrystals.

In our opinion, the formation of aragonite layers was the result of redeposition from the shelf of the decomposition products of aragonitic molluscan shells (*Dreissena* and *Monodacna*). In fact, elongated "needlelike" fragments, comparable in size to particles of aragonite layers form upon their decomposition (see Fig. 2d). In post-Neoeuxinian sediments of the western and northern shelf and continental slope different stages of mollusc decomposition and formation of aragonite "crystals" are visible in thin section, with this phenomenon occurring on a large scale at the beginning of ancient Black Sea time. In all probability, the higher than usual hydrodynamic activity during postglacial transgression of the Black Sea following extensive resettlement of Neoeuxinian molluscs over the flooded part of the shelf resulted in an intense destruction of aragonitic shells (with a formation of the above-described particles). Later they were transported to the deep-water part of the sea, where they were deposited at the bottom. The character of the mineral grains within the layers suggests that they were precipitated from water as ordinary fragmental particles.

Terrigenous carbonates have been quite reliably determined in sediments of many regions of the Black Sea. They are represented to varying degrees by rounded fragments of such calcareous rocks as microcrystalline, biogenic, oolitic limestones, dolomites, marl, and less commonly siderites as well as by crystals of calcite, often with well developed cleavage, and of dolomite and by their fragmental material.

In microscopic studies with a binocular microscope terrigenous carbonates have been detected in >0.1-mm fractions in the form of individual particles and aggregates. In thin-section study they have been determined on the basis of distinctive petrographic features and are concentrated among the sand and silt particles (see Fig. 2e).

The mineralogically terrigenous carbonates are composed of calcite and dolomite. Calcite in modern and ancient Black Sea sediments has been reliably determined in samples where there are few biogenous carbonates. In Neoeuxinian sediments where biogenous carbonates are composed of aragonite, calcite ( $d/n = 3.03 \text{ \AA}$ ) in the coarse-grained fractions has a terrigenous origin.

The areas of occurrence of terrigenous carbonates are generally closely associated with the areas of development on the shores of the Black Sea of calcareous rocks as a result of the erosion of which they enter the basin. The highest concentrations of them are on the shelf and continental slope near the Caucasus where Cretaceous-Paleogene carbonate flysch is exposed, near the Crimea (between Cape Tarkhankut and Alushta) where Jurassic, Cretaceous and Neogene limestones are widespread on land, and in the area between Cape Kaliakra and the eastern shores of Turkey where Mesozoic-Cenozoic limestones and dolomites crop out.

In modern and ancient Black Sea sediments the highest concentrations of terrigenous carbonates comparable in importance to those of biogenous carbonates are predominantly on the shelf. In the western half of the basin there is a higher than usual dolomite content. As the sediments recede from the shore and thin, the importance of the terrigenous carbonates rapidly decreases, and in the deep-sea muds they are identified on mineralogical analysis among light minerals of the silt fraction [2, 7, 8].

In the upper profile of Neoeuxinian sediments the role of terrigenous carbonates increases. In the above regions in the coarser-grained fractions they are often the principal carbonates. However, unlike the younger horizons, their importance increases even in the sediments of the upper zone of the continental slope. Downward in the section of Neoeuxinian sediments the absolute content of the terrigenous carbonates decreases with a decrease in their carbonate content, although their relative importance remains high. The predominant mineral in most of the regions is calcite, but in the western half of the sea the dolomite content is often comparable to that of calcite, and occasionally dolomite is even the principal mineral.

Chemogenic carbonates are second in importance to the two above carbonate types. In Black Sea sediments they are represented by two varieties: diagenetic and sedimentary.

Diagenetic carbonates have been described by Butuzova and Trimonis [2, 7]. These authors have classed them with the calcite crystals found among fine silt particles in deep-sea sediments. However, an identification of diagenetic carbonates, particularly in post-Neoeuxinian sediments, has been made difficult because of their small amounts and similar mineralogy with biogenous carbonates.

Diagenetic carbonates in deep-sea sediments have been discovered by us in coccolith oozes in the form of well-edged calcite crystals less than 2  $\mu\text{m}$  in size (see Fig. 2f). In addition, white calcite concretions less than 2 mm in size have been observed in ancient Black Sea sapropelic muds. Apparently, part of the carbonates in Neoeuxinian sediments, which is composed of fine pelitic calcite, belongs to diagenetic formations, although it is difficult to assess its role.

In shelf deposits diagenetic carbonates participate in cementation of terrigenous and shelly beach sediments and form incrustated layers on the rocks and molluscan shells exposed on the sea floor. The shallow-water deposits are cemented with aragonite and calcite. The cement, according to microscopic studies with the scanning electron microscope (SEM), consists of aragonite needles, which envelop the quartz and other mineral grains, and of prismatic calcite crystals, which cement the molluscan shells and mineral grains. On limestones which crop out in the vicinity of Cape Kaliakra we have observed yellowish-green films of semicrystalline magnesite (3-5%  $\text{MgCO}_3$ ).

Sedimentary carbonates have not been found in modern or ancient sediments of the Black Sea. The acidic geochemical medium in the water layer, determined by the presence of free hydrogen sulfide in the waters, as well as the lower (+9°C) water temperature have prevented their precipitation. However, in a section of late Neoeuxinian muds, as reported previously [4, 5], a uniform layer of fine-grained calcareous ooze (50-80%  $\text{CaCO}_3$ ), several tens of centimeters thick, has been observed in the western deep-sea basin. The carbonates in it are represented by calcite crystals of predominantly coarse pelite size (see Fig. 2g). A characteristic feature of them is the considerable dissolution of the faces and even of the edges, as a result of which the internal structure of the crystals is exposed. These layers contain practically none of the dolomite abundant among terrigenous carbonates. It is likely that the carbonates of synchronous deep-sea sediments of other areas of the Black Sea, in particular the Kerch' region where the carbonate content of the muds increases to 30%, also have a sedimentary origin.

In the northwestern and western areas of the shelf the pelitic fraction in many of the cores of late Neoeuxinian sediments contains 50% and more of fine crystalline calcite, which most likely owes its origin to the process of direct precipitation from sea water.

\* \* \*

The material studied by us shows that throughout the late Quaternary carbonate accumulation in the Black Sea has undergone considerable change, which has resulted in certain combinations of different genetic types of carbonates in sediments.



In the last glacial maximum, as a result of a sharp decline in the level of the Black Sea, the shelf was practically nonexistent. Thus, biogenous carbonate accumulation in the brackish- and cold-water environment of the Neoeuxinian lake basin was negligible; terrigenous carbonates in combination with their diagenetic varieties were predominant in the slightly calcareous terrigenous sediments.

As the glacier shrank and the sea level rose owing to warmer conditions and intensification of chemical weathering processes on land, an ever increasing amount of dissolved  $\text{CaCO}_3$  began to enter the basin, as noted by the higher total carbonate content in Neoeuxinian sediments upward in the section. Although the process of biogenous carbonate accumulation intensified toward the end of the Neoeuxinian, the influx of dissolved carbonates exceeded the capacity of organisms to precipitate them from water. Thus, as conditions became warmer and drier, the waters became supersaturated with respect to  $\text{CO}_2$ , and part of the carbonates began to be precipitated chemogenically. At the end of the Neoeuxinian a similar process led to a mass chemogenic deposition of  $\text{CaCO}_3$ . As a result, a layer of chemogenic marllike muds formed in the western half of the Black Sea where the bulk of dissolved substances entered from land, and the carbonate content of the sediments in the eastern half of the basin increased. At this time chemogenic sedimentation began to predominate among the carbonates, and biogenous and terrigenous carbonates were accumulated in the sediments in subordinate amounts.

In post-Neoeuxinian time the environmental setting of the Black Sea changed. As a result of the established association with the Mediterranean, the waters of the Black Sea became salinized. Large colonies of Mediterranean species of lime-secreting organisms settled in the Black Sea, and their productivity increased substantially. Carbonate deposition in the basin began to be completely controlled by the biogenic process, as a result of which diverse remains of its planktonic and benthonic organisms, which fed on all the dissolved carbonate that entered the sea from land, accumulated in the sediments. Thus, both shelf and deep-sea biogenous carbonate deposits began to be formed on a large scale, and the carbonate content of the terrigenous facies increased considerably.

Although the role of terrigenous carbonates remained the same, their relative importance declined sharply. The chemogenic sedimentation process ceased in post-Neoeuxinian time because of the lack of original material and because of the formation of an aggressive hydrogen sulfide environment. The contribution of diagenetic carbonates to carbonate sedimentation in the Black Sea was very small and has no real significance in the general process of carbonate accumulation.

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FORMATION AND ARRANGEMENT OF COASTAL-MARINE PLACER DEPOSITS  
IN THE REGION OF SCANDINAVIAN GLACIAL COVER DEVELOPMENT\*

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UDC 553.068.34:551.32

On the basis of materials that have been accumulated up to the present time, the role played by shore morphology, the rate and sign of vertical displacement of the coast, the character of detrital material input into the coastal zone, and the hydrodynamic regime is clarified in the formation and arrangement of coastal-marine placer deposits. Reasons for the differences in composition of mineral associations in placer deposits of the Baltic shield and Russian plate are established.

In Pleistocene time, following the covering glaciations, marine transgressions developed which encompassed significant areas of the northern part of the European continent during the period of their maximum distribution. In the coastal zone of basins, concentration of ore and accessory minerals should have occurred in a favorable geomorphic and hydrodynamic environment. However, Pleistocene coastal-marine placer deposits which formed before the last glaciation have not been detected up to this time. It is evident that they were assimilated by the glacial covers and dispersed in the course of movement of the ice mass. Only placer deposits which are correlated to Holocene marine sediments are completely represented. They developed on the shores of the North, Baltic, and White seas, and have been studied in detail within the limits, as a rule, of short segments. These placer deposits are exploited in the GDR, and they present practical interest in Denmark and Poland. Their exploitation may also prove to be profitable in the USSR on the southern coast of the Kol'sk peninsula [14]. Mineral resources in the indicated formations are: magnetite, ilmenite, zircon, rutile, garnet, staurolite, kyanite, and sillimanite; however, for the present, only magnetite, ilmenite, and zircon are extracted. This article systematizes the materials that have been accumulated up to the present time, with the aim of clarifying the formation conditions and the rules governing the distribution of placer deposits.

Formation of coastal-marine placer deposits is determined by the morphology of the coastal zone, the rate and sign of tectonic displacements of the coasts, the character of input of detrital material into the coastal zone, and the hydrodynamic regime. The composition of the generated concentrations of heavy minerals depends primarily on that of the parent deposits. The following data are indicative of this. Any significance to the scales of accumulation of heavy minerals in late glacial marine sediments are undetected. In the period of degradation of the last glaciation cover, as well as of the more ancient cover, the continent was uplifted fairly intensely in proportion to removal of the glacial load. Nonetheless, earlier accumulations of deposits in the coastal zone were not only eroded by the sea, but sedimentary thicknesses were also accumulated which occupy large areas. This was caused by the introduction of significant masses of pebble-sand and silt-clay size fragments into the basins by melted glacial waters. Naturally, such a paleogeographic and tectonic environment was extremely unfavorable for the separation of heavy minerals. Their concentration occurred only then, when the rate of uplift was lowered and the volume of detrital material advancing into the basins was decreased, that is, post-glacially. Formation of placer deposits in Holocene time began in the Atlantic period and continued down to the present time. It is necessary to note that in the pre-Littorina stage of most recent motion, the regions of the North, Baltic, and White seas as a whole experienced uplift. In the late Littorina stage, the motions were differentiated by sign. The coasts of a large part of the Soviet Baltic region and the Kol'sk

\*In this article, placer deposits are understood to be not only occurrences of mineral resources, but also increased concentrations of other heavy minerals in sandstones.

Geological Institute, Kol'sk Branch, Academy of Sciences of the USSR, Apatity. Translated from *Litologiya i Poleznye Iskopaemye*, No. 1, pp. 31-40, January-February, 1987. Original article submitted July 6, 1985.

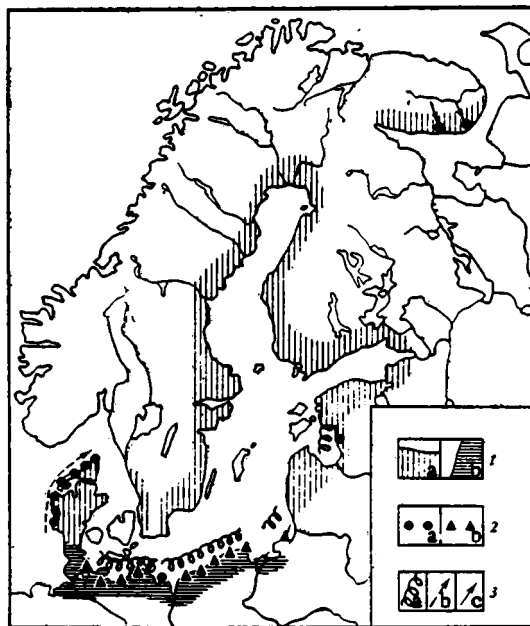


Fig. 1. Scheme of the distribution and formational environment of coastal-marine placer deposits. 1) Coasts, uprising (a) and subsiding (b) in middle and late Holocene; 2) placer deposits of uprising (a) and subsiding (b) coasts; 3) sources supplying detrital material into the coastal zone: a) swell, b) longshore current, c) river.

peninsula continued to be uplifted, while the coasts of the FRG, GDR, and Poland generally began to subside [3, 12, and others]. This circumstance makes it possible to distinguish and characterize two groups of placer deposits. It is possible to place placer deposits which formed under conditions of uplifting of coastal regions in the first group, and placer deposits occurring on subsiding coasts into the second. Their distribution is shown in Fig. 1.

Formation of the first group of placer deposits began earliest on the coast of the Baltic Sea. Littorina concentrations of mineral resources were established and studied in fair detail on the eastern shore of the Gulf of Riga [10, 11, 17] and in the coastal zone of Uzed Island in Pomorsk Bay [23 and others]. Based on the data of Latvian investigators, the Littorina accumulation terrace is comprised of fine- and medium-grained sands with layers and lenses of coarse-grained and gravelly sands with occasional pebbles. The zone enriched in heavy minerals was correlated to two shore embankments, which are located at the inner edge of the terrace adjacent to the town of Ainazhi. Concentrates of heavy minerals lie at a depth of 1.5 m, and form two lenticular layers up to 0.35 m in thickness. Sheets 0.5 to 7 cm thick that are significantly enriched and depleted in heavy minerals alternate in these layers. The width of the zone comes to 20-30 m, and the length reaches several kilometers. In the Lemme-Piiskop region an analogous zone of enriched sands, localized within the limits of the shore embankment, lies at a depth of 1.5-2 m and is represented by 3-4 layers with an average thickness of 0.5 m. These layers are similar in structure to those described above, and are distinguished from one another by thicker layers of barren sand. The zone has a width of 10-15 m and is traceable over 1.8 km. A correlation of the concentrations with gravel-pebble interbeds is also observed. In grain-size composition the concentrations of heavy minerals are undistinguished from general Littorina sands. The content of the heavy fraction in fine- and medium-grained sands with macroscopically visible concentrations varies from 4 to 60%, while in sands which lie above and below the layers of concentrations, without visible accumulations of heavy minerals, it varies from 1.5 to 5%. A high average content of the heavy fraction, equal to 11% (with variations from 2.1 to 27%), is characteristic for gravelly sands. Littorina sands with increased heavy mineral content (up to 12%) are also detected by V. G. Ul'st [16] at the inner edge of the terrace on the shore between Ventspils and Kolka.

The second region where placer deposits of *Littorina* and similar age are distributed is the shore of Uzed Island in Pomorsk Bay. These placer deposits are represented by fine-grained sands and lie on a moraine or older marine Holocene sands. Zones of enrichment, detected by K. Kail'khak and E. Vasmund adjacent to Al'bek, are correlated to beach at the *Littorina* cliff and shore embankment. The width of the enriched zone at the cliff varies from 10 to 60 m, reaching 26 m on the average; its length reaches 1.6 km. Observed in its section are both massive concentrated layers up to 0.1 m in thickness, and layers in which interbeds that are enriched and depleted in heavy minerals alternate, with a total thickness of up to 0.5 m. Layers in coastal embankments that are analogous to the above described layers vary in thickness from 0.1 to 0.3 m. In section they alternate with barren sand layers ranging in thickness from 0.4 to 1 m. The heavy mineral content in the massive layers reaches 70-80%, while in the alternating layers it reaches 4-50%. Somewhat younger placer deposits are located adjacent to Tsinovits and Tsempin in a depression of a former erosion area. The enrichment zone reaches 2 km in length, and the thickness varies from 0.07 to 0.35 m.

*Littorina* placer deposits of the coastal Soviet pre-Baltic area in the GDR were formed from detrital material that was mobilized by erosion. The poorly sorted deposits of the Baltic glacial lake were primarily subjected to wave reworking. Correlation of the concentrations to the inner edge of the *Littorina* terrace, which was established on the coasts of Latvia and Estonia, is explained thusly: the slowest growth of accumulative forms occurs namely at the start of the stage of coastal development, and the most favorable conditions for formations of placer deposits are ultimately created [16].

In the late *Littorina* period of the Holocene on the portion of the Baltic coast that continued to experience uplift, sediments accumulated only as a result of erosion. With time, in proportion to the decrease in the rate of coastal uplift, the intensity of erosional-accumulative processes fades, and in addition, primarily all of the deposits from the underwater coastal slope of basins from preceding stages in the development of the Baltic that are poorer in heavy minerals are reworked in the wave-cut zone. In connection with the indicated circumstances, at the present time on beaches of eroded and relatively stable coasts, zones that are significantly enriched (up to 86%) in heavy minerals in fine- and medium-grained sands are extremely insignificant in size. On the shores of Estonia, Latvia, Lithuania, and the southern half of the Kaliningrad area, their width reaches 3 m, their extent may be several tens of meters, and their thickness varies from 2 to 25 cm [9, 10, 17].

Marked negative factors are apparent on the sandy coasts that were rising during Holocene of all of the marine basins which lie in the area where Scandinavian glacial cover developed. Accordingly, late *Littorina* placer deposits within the limits of these shores formed only in cases where rivers or marine currents supply fresh detrital material to the coastal zone. Thus, on the northern shore of the White Sea, fine- and medium-grained sands which are significantly enriched in heavy minerals are concentrated at near-outlet portions of rivers and formed continuously because of alluvium over the extent of roughly the last two thousand years. Holocene placer deposits here are correlated to the frontal part of large coastal embankments that are most distinctly expressed in relief, and to the beach at the cliff. Their extent varies by hundreds of meters, sometimes exceeding 1 km, their width comes to 4-12 m, and their thickness varies from 0.2 to 0.5 m. The heavy fraction content in concentrates of coastal embankments varies from 4 to 70%, and in concentrates which lie at the cliff it reaches 89%. Recent placer deposits\* in the examined region are attracted to level parts of the beach and to the coastal embankment. They are similar to Holocene deposits in size and heavy mineral content [5]. As a result of reworking of detrital material supplied by longshore currents in the wave-cut zone, placer deposits are forming at the present time on the coast of the North Sea. They are located on high parts of the beach of the northern (principally) and western low sandy shore of the Jutland peninsula [10]. The total extent of the placer deposits comes to 25 km. The content of heavy minerals in concentrates varies from 4 to 97%. In all, approximately 100,000 tons of concentrate are concentrated in placer deposits.

Placer deposits of the second group, which are correlated to beaches and littoral coasts that experienced submersion in middle and late Pleistocene, are distributed extremely widely. They are known and studied in some detail on the coasts of Poland, the GDR, FRG, Denmark, and the Soviet pre-Baltic [8, 9, 18-20, 22, 24, and others]. Placer deposits formed both on erosional-

\*Here and farther on, all placer deposits which formed over the course of the last ten thousand years and which emerged from the sphere of influence of wave-action due to modern sea level are designated Holocene, while Recent placer deposits are found within the limits of the wave-cut zone.

accumulative, and on accumulative coasts. On the first type of coast they are found under the influence of even insignificant sea level fluctuations, and therefore they are constantly being reconstructed, sometimes enriched, sometimes depleted in heavy minerals. On a wide beach, the concentration zone, which lies at the cliff, is redeposited only by a significant increase in sea level. On accumulative coasts, as well as on erosional-accumulative coasts, the concentration zones almost always lie on the surface. In some places they are subjected to the influence of hydrometeorological factors, in some places they temporarily appear to be beyond this action. Placer deposits have a thickness of 5-100 cm, and are represented by fine- and medium-grained well-sorted sands, containing 5-99% heavy minerals. Frequent concentrated interbeds are observed in section with thicknesses of 1-15 mm, and rarely thicker. The width of the enrichment zone reaches 20 m, and the length varies from several hundreds of meters to a few kilometers. In distinction from other sedimentary occurrences, recent placer deposits that have been depleted or destroyed by natural means, from both erosional-accumulative and accumulative coasts, are regenerated by the conditions of conservation of near-shore configuration and by the coastal-dynamic processes occurring in the wave-cut zone [18, 21, 22]. It is evident that the wide distribution of recent placer deposits forming as a consequence of coastal abrasion in a subsiding region depends on the fact that here primarily more ancient Holocene marine deposits are subjected to wave reworking, among them those that are enriched in heavy minerals.

The above described placer deposits of both groups as a rule lie on more ancient marine sediments, seldom on continental deposits of the glacial paragenetic series. They were formed as a result of reworking in the coastal zone primarily of alluvia supplied by water currents or longshore currents, or of underwater deposits. The original material is represented by various differentiates of glacial formations. This is indicated in particular by the similarity of mineral associations of moraines and placer deposits [9, 18, and others]. Comparison of the mineral composition of the heavy fraction of the indicated formations on a quantitative level presents significant interest. To avoid random conclusions, it is advisable to conduct a statistical classification of the data. We dwelt on the amalgamation of analytical results into three groups based on the degree of mineral resistance to weathering agents. In agreement with the works of G. S. Momdzhii [13] and A. A. Kukharevskii [7], the resistant minerals include magnetite, ilmenite, hematite, rutile, leucoxene, perovskite, sphene, monazite, kyanite, tourmaline, and others; the intermediate minerals include amphibole, pyroxene, biotite, and chlorite.

It is necessary to note that G. S. Momdzhii [13] considered magnetite and perovskite non-resistant minerals, while A. A. Kukharevskii [7] considered them resistant. Both of these appraisals are true, but in completely specific natural environments. In a temperate humid climate, the indicated minerals are resistant in the formation of hydromica weathering crust. In tropical climatic conditions and formation of kaolinite or laterite weathering crusts, they decompose [2 and others]. We agreed it is possible to place magnetite and perovskite in the group of resistant minerals on the basis that immediately before the Quaternary period, rock weathering in the area of Scandinavian glacial cover development occurred in a moderately humid climatic environment [15].

It is necessary to note that all of the mineral resources extracted from alluvial deposits at the present time are concentrated in the first and second groups. Their density and resistance to abrasive actions are higher than the minerals of the third group. This circumstance is extremely significant, since in the process of placer deposit formation, other conditions being equal, minerals are differentiated by the indicated criteria.

Let us proceed to consideration of actual material. Relations of the three mentioned groups of minerals in moraine and coastal-marine placer deposits are reflected in the respective diagrams (Figs. 2 and 3). Analysis of the first diagram shows that two significantly different mineral associations are characteristic for a moraine of the covering glaciation. In one, the typical Baltic shield moraine, nonresistant minerals dominate as a rule; their content varies from 45 to 92%. Intermediate minerals make up 4-49% (in only one case 73%), while resistant minerals comprise 3-26%. The composition of this moraine corresponds completely to that of the original rocks: products of Neogene hydromica and Quaternary weathering of metamorphic and igneous formations, and sediments arising from redeposited weathered material. Other proportions are observed in the other association, that of the Russian plate covering moraine. The nonresistant minerals generally comprise less than 50%, with a variation in the content from 14 to 57%; the intermediate minerals make up 18-51%, and the resistant make up more than 20%, with a variation of 6 to 68%. The increase in the portion of intermediate and resistant minerals in the second type of moraine is connected with the fact

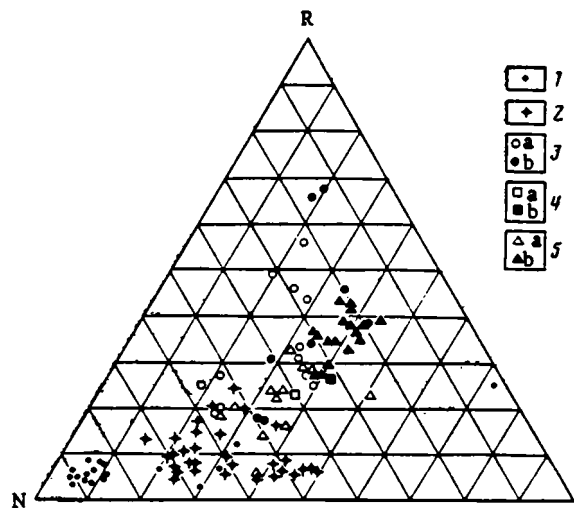


Fig. 2. Diagram of the heavy fraction mineral composition of the Valdaisk glaciation moraine (compiled from data of the authors, A. V. Raukas, A. S. Sabbaitova, A. Yu. Klimashauskas, and I. M. Ekman. Baltic shelf: 1) Kol'sk peninsula (0.25-0.1 mm fraction); 2) western part of Karelia (0.1-0.05 mm fraction). Russian platform with covering of Phanerizoic deposits: 3) Estonia (a) 0.25-0.1 mm frac., b) 0.1-0.5 mm fraction); 4) Latvia (a) 0.25-0.1 mm fraction, b) 0.1-0.5 mm fraction); R: resistant minerals, I: intermediate minerals, N: non-resistant minerals.

that within the limits of the Russian plate, the glacier assimilated a large volume of sedimentary deposits (mainly differentiates of phanerozoic weathering crusts of crystalline rock) and their Neogene weathering products, the heavy fraction of which in practice contains allo-genic minerals of the two mentioned groups. The question of the formation of the material composition of the Baltic shield and the Russian plate moraines are considered in detail in [6].

The mineral associations of the placer deposits of the indicated regions are also significantly distinguished. Points of the analyses corresponding to them are individually arranged on the diagram. In concentrations of heavy minerals distributed on the Baltic shield territory, the nonresistant minerals predominate in large part (40-90%), intermediate minerals come to 8-50%, and resistant minerals come to 3-23%. In the heavy fraction of placer deposits from the Russian plate, the nonresistant mineral content varies within the limits of 0-33%, (in one analysis 49%), intermediate minerals range from 6-79%, and resistant minerals range from 13-94%.

From the cited data it follows that placer deposits from the Kol'sk peninsula and the Russian plate are higher in intermediate and resistant minerals and correspondingly lower in non-resistant minerals, than are the moraines of other territories. Thus, minerals are accumulated in the placer deposits which are distinguished by high density and abrasion resistance. For clarification of the behavior of the primary minerals in the process of placer deposit formation, we turn to the results of mineralogic investigations of natural concentrations. Representative sampling data on the composition of these are shown in Table 1. Their analysis shows that amphiboles and pyroxenes are present in the greatest quantity in the heavy fraction of the Baltic shield placer deposits. The total content of garnets, ore minerals and epidote is significantly lower; while the garnet content always exceeds that of the ore minerals. As a rule, less than 1% of the concentrates are composed of zircon and rutile. In the placer deposits of the Russian plate, garnets and ore minerals dominate. The fact that in single regions the garnet content is significantly greater than the ore mineral content, at the same time that in other regions minerals of the indicated groups predominate alternately is noteworthy. The portions of the remaining useful minerals (zircon and rutile) only occur as fractions of percent or a few percents. Anomalously high (10%) zircon contents are char-

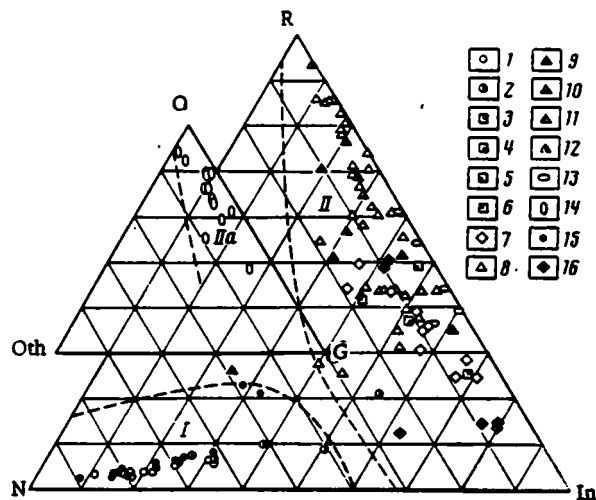


Fig. 3. Diagram of the mineral composition of the heavy fraction of concentrates from coastal-marine deposits. Recent formations. Coast of the White Sea: 1) near the mouth of the Varzuga River; 2) near the mouth of the Pyalitsa River. Coast of the Baltic and North Seas and Baltic lakes [9]: 3) between Klaipeda and the Latvian boundary; 4) overflow of Kurshyu-Nyarai; 5) Sambiisk peninsulas; 6) Gulf of Kurshyu-Mares; 7) coast of Latvia [17]; 8) Jutland peninsula [19]; 9) Zelandiya Islands [19]; 10) Fyn Islands [19]; 11) Lollannd Island [19]; 12) Bornholm Island [19]; 13) Mecklenburg Bay [20]; 14) Schleswig-Holstein [21]; Holocene placer deposits. Coast of the White Sea: 15) near the mouth of the Varzuga River. Coast of the Baltic Sea: 16) coastal precipice at the shore of the Irbe River and the Gulf of Riga [10, 17]; I) composition field of placer deposits of the Baltic shield; II, IIa) area of development of sedimentary cover of the Russian platform (R: resistant minerals, In: intermediate, N: non-resistant, O: ore, G: garnet, Oth: other).

acteristic of placer deposits from the coast of the Jutland peninsula. The prevalence of garnets over ore minerals, established in every placer deposit of the region, the dominance of amphiboles and pyroxenes in the concentrates on the coast of the Kol'sk peninsula, and the high zircon content in the placer deposits of the Datsk coast are predetermined by the mineral composition of the parent deposits. Regarding the predomination of ore minerals in sampling of concentrate from the Jutland coast, this is a consequence of ideal mineralogic differentiation, the path of which will be spoken of more thoroughly below. Another consequence of differentiation is a decrease in the content of epidote, amphiboles, and pyroxenes in proportion to an increase in the output of the heavy fraction (see table).

By the method of multiple correlations of data from forty-four analyses of placer deposits from the Kol'sk peninsula which were correlated to shore embankments, it is established that the heavy mineral content is closely connected with the primary characteristics of grain distribution by coarseness: to average size, sorting coefficients, asymmetry, and kurtosis. The total correlation coefficient comes to 0.772. The content of the heavy fraction is higher the better the sorting of the sediments and the more asymmetric the distribution. These statistical connections become understandable, if one considers that the maximum of distribution of heavy minerals in the coastal deposits is always shifted towards the side of the finer classes of the relatively corresponding maximum of the light fraction minerals. It is therefore entirely natural, that in porportion to the distribution of minerals of the indicated fractions in the wave-cut zone, sediment sorting is improved, and in addition, asymmetry in

TABLE 1. Content of Primary Minerals in Various Aged Concentrations from Sands of Various Coastal Regions

| Sample number                                                                | Output of heavy fraction, % of sample mass | Mineral contents, % of total mineral fraction |        |        |        |                          |                               |        |
|------------------------------------------------------------------------------|--------------------------------------------|-----------------------------------------------|--------|--------|--------|--------------------------|-------------------------------|--------|
|                                                                              |                                            | ore minerals (illmenite, magnetite, etc.)     | garnet | zircon | rutile | amphiboles and pyroxenes | minerals of the epidote group | others |
| Littorina deposits of the Gulf of Riga [10]                                  |                                            |                                               |        |        |        |                          |                               |        |
| 64                                                                           | 2,22                                       | 9,46                                          | 62,61  | 0,90   | 0,45   | 18,06                    |                               | 8,52   |
| 8                                                                            | 11,57                                      | 13,14                                         | 76,49  | 1,04   | —      | 7,61                     |                               | 1,72   |
| 50                                                                           | 28,12                                      | 12,80                                         | 73,41  | 0,60   | 0,60   | 4,19                     |                               | 2,40   |
| 41                                                                           | 42,62                                      | 11,31                                         | 79,61  | 1,01   | 0,61   | 4,78                     |                               | 2,68   |
| Subatlantic sands of the southern coast of the Kol'sk peninsula              |                                            |                                               |        |        |        |                          |                               |        |
| B-14/1                                                                       | 12,3                                       | 1,9                                           | 9,8    | 0,3    | Trace  | 64,4                     | 9,0                           | 14,6   |
| B-14/3                                                                       | 39,5                                       | 4,4                                           | 14,8   | 0,5    | "      | 62,6                     | 9,5                           | 8,2    |
| B-14/7                                                                       | 68,5                                       | 4,5                                           | 19,3   | 0,4    | "      | 58,5                     | 10,5                          | 6,8    |
| B-44/3                                                                       | 88,9                                       | 16,2                                          | 25,1   | 1,2    | 0,1    | 45,1                     | 6,9                           | 5,4    |
| Recent sands of the southern coast of the Kol'sk peninsula                   |                                            |                                               |        |        |        |                          |                               |        |
| 73-25/6                                                                      | 8,9                                        | 5,8                                           | 20,7   | 0,2    | Trace  | 61,4                     | 4,6                           | 7,3    |
| 73-25/3                                                                      | 37,2                                       | 7,6                                           | 32,1   | 0,2    | 0,1    | 49,8                     | 4,8                           | 5,4    |
| 73-25/7                                                                      | 68,2                                       | 19,5                                          | 50,8   | 0,2    | 0,1    | 23,5                     | 2,1                           | 3,8    |
| Recent sands of the western and northwestern coasts of the Jutland peninsula |                                            |                                               |        |        |        |                          |                               |        |
| 9                                                                            | 33                                         | 31                                            | 33,12  | 3,45   | 0,69   | 9,66                     | 15,87                         | 6,21   |
| 41                                                                           | 64                                         | 26                                            | 35,52  | 5,92   | 0,74   | 13,33                    | 15,54                         | 2,95   |
| 39                                                                           | 78                                         | 28                                            | 37,44  | 12,96  | 0,72   | 10,80                    | 5,76                          | 4,32   |
| 35                                                                           | 94                                         | 50                                            | 32,50  | 8,50   | 1,00   | 1,50                     | 4,00                          | 2,50   |
| Recent sands of Mecklenburg Bay [20]                                         |                                            |                                               |        |        |        |                          |                               |        |
| 1                                                                            | 77                                         | 25                                            | 49     | 1,0    | 0,2    | 7,0                      | 5,5                           | 13,0   |
| 2                                                                            | 83                                         | 34                                            | 53     | 4,5    | 0,6    | 0,6                      | 1,9                           | 5,3    |
| 3                                                                            | 96                                         | 46                                            | 48     | 1,4    | 0,2    | 0,7                      | 1,3                           | 3,1    |

the distribution of detrital particles by sizes increases (but, it is evident, not in every possible range in the variation of the heavy fraction content). It is also established by correlation analysis that with increased output of the heavy fraction, the relative content of minerals whose density exceeds 3.5 g/cm<sup>3</sup> grows: garnet, sphene, magnetite, illmenite, rutile, zircon, monazite, loparite, staurolite, and kyanite, while the content of minerals with densities on the order of 3-3.5 g/cm<sup>3</sup> decreases: pyroxenes, amphiboles, and sillimanite [4]. An analogous result is obtained by analysis of materials cited in an article on recent placer deposits of Denmark [19]. Concentration of the useful components of placer deposits is accomplished as a result of natural concentration: the sifting of heavy minerals into the base of the active layer of the alluvia and the subsequent rolling away in the direction of the sea of grains of quartz, feldspars, and the heavy fractions that have a small density [1, 20, and others]. This process is developed more intensely the smaller the asymmetry in the velocities of the forward and return surf flows. Hydrodynamic parameters are varied often during the formation of placer deposits, but within narrow limits. As a consequence of this, repeated redeposition of alluvia occurs, which contributes to the accumulation of ore and accessory minerals [5].

Sedimentary and glacial deposits were reworked in the coastal zone of all of the marine basins, spreading over the length of the Quaternary period within the continental limits. In connection with this, minerals of the heavy fraction were undoubtedly concentrated in distinct portions of the basins under favorable conditions. Pleistocene placer deposits, evidently, were destroyed by the glacial covers, while Holocene placer deposits, which formed after the last glaciation, developed fairly widely. Results of study of Holocene placer deposits indicate the following.

Significant concentration of heavy minerals occurs primarily on shallow accumulative and erosional-accumulative sandy coasts for low velocities of vertical coastal displacement. Input of fresh detrital material into the coastal zone is a necessary condition for the formation of placer deposits. In the pre-Littorina stage the most recent motions were moderating at the time the entire region, which in the recent past was occupied by glacial cover, underwent isostatic uplift. At the end of this stage on coasts which were uplifting with small velocity, placer deposits formed as a consequence of intense erosion, primarily of the late



glacial sediments. They were correlated to the inner edge of the accumulative terraces, since, as shown by V. G. Ul'st, it is precisely in the initial stage of development that the accumulative forms grow most slowly, and in connection with them the most favorable conditions for differentiation of detrital material are created. In late Littorina time, the most recent motions were differentiated by sign. On the coasts which are continuing to rise, in view of the significant decrease in the intensity of erosional-accumulative processes, placer deposit formation occurs only on the portions of the coasts within whose limits alluvia is supplied by rivers or longshore currents. On the coasts whose uplift alternated with subsidence, placer deposits were formed owing to erosion and redeposition in the coastal zone of sediments (including those enriched in heavy minerals) which were accumulating in the preceding period of regression. They are distributed extremely widely (see Fig. 1).

Concentrates from the coastal-marine deposits of the Baltic shield and the Russian plate are clearly distinguished by the mineral composition of the heavy fraction. Significantly more minerals that are nonresistant with respect to weathering agents are found in the former, which reflects the specifics of the composition of the original pre-Quaternary shield and plate, and correspondingly intermediate heavy mineral reservoirs which in both regions are deposits of the glacial paragenetic series. Concentration of the useful components of placer deposits is accomplished by means of natural concentration.

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#### EVOLUTION OF BAUXITE-FORMING PROCESSES IN THE PHANEROZOIC

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UDC 553.492:551.12

By correlating data on the mineral parageneses of Phanerozoic bauxite deposits with other indications of change over time it is shown that the basis for the evolution discovered was a radical transformation in the conditions of bauxite formation and in a number of important properties in weathering products.

It is known that economic bauxite deposits are characteristic only of the Phanerozoic Eon of geologic time. However, the evolutionary approach to the analysis of rock and ore-formation processes traditional in geology has not yet been applied widely enough to this interesting and important product of exogenesis. At the same time, it is clear that the correct solution of the problem of the evolution of bauxite formation (or at least an essentially correct understanding of the driving forces of this evolution) can not only throw additional light on many hotly disputed aspects of the genesis of bauxites, but also provide new regional criteria for evaluating bauxite deposits of different ages [4, 6, 7, 12, 13]. Furthermore, bauxites are one of the most striking and extreme products of humid climate lithogenesis on Earth. For this reason, tracing the evolution of bauxite-formation conditions may also help in revealing the changes over time of a more widely manifested transformation of mineral matter where lithosphere, atmosphere, and biosphere interface, as well as in evaluating the evolution of the physicochemical parameters of ancient atmospheres.

We shall confine ourselves primarily to the available data for changes of the material composition of bauxites throughout the Phanerozoic. For example, it has been known for decades now that the older the bauxites, the greater the extent to which the low-water-content aluminum hydroxides diaspore and boehmite predominate in them. This was clearly shown in diagrammatic form by Gorbachev [10].

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All-Union Aluminum and Magnesium Institute, Leningrad. Translated from *Litologiya i Poleznye Iskopaemye*, No. 1, pp. 41-50, January-February, 1987. Original article submitted February 19, 1986.

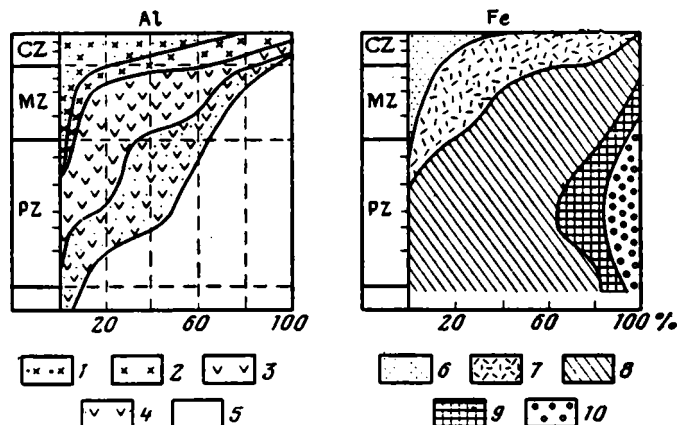


Fig. 1. Distribution in time of major parageneses of aluminum and iron minerals in bauxites overlying carbonate and mixed aluminosilicate-carbonate substrates (from Bardossy [3] with additions). 1) Gibbsite; 2) boehmite-gibbsite; 3) boehmite; 4) diaspore-boehmite; 5) diaspore, diaspore-corundum, and corundum; 6) goethite; 7) hematite-goethite; 8) hematite; 9) chamosite, chamosite-hematite; 10) others.

An analogous picture arises in analyzing the distribution of goethite and hematite in bauxites. For example, in Cenozoic and, to a lesser degree, Mesozoic bauxites goethite is so widely developed that it causes difficulties in processing them due to the complexity of the technical processes their presence in the ore necessitates. In Paleozoic bauxites goethite is only a minor component, and in deposits of pre-Carboniferous time this mineral is not detected at all.

Less differentiated are the changes over time of the silica-containing minerals of bauxites. For example, in Cenozoic and Mesozoic bauxites this element is found only in kaolinite and/or quartz, and chamosites are present in only very limited amounts, and only in regions that have been subjected to secondary reduction processes. In Paleozoic bauxites, however, chamosite is widely developed in addition to the kaolinite, and in a number of sections its quantity far exceeds that of the kaolinite, the the point that the latter may completely disappear.

A quantitative estimate of the change over time of the chemical (up to 48 elements) and mineral composition of the bauxites and their parent rocks from the Paleozoic to the Cenozoic based on sampling practically all the major deposits in the USSR and about 70% of the bauxite deposits of the world is given in [7 and others].

Analysis of this information shows that with the passage of time from the Paleozoic to the Cenozoic there is a regular change in both the chemical and mineral composition of the bauxites. It is manifested in a decrease in the average content and the concentration coefficients of about 80% of the elements studied. At the same time the number of low-water-content and anhydrous oxide and hydroxide aluminum and iron minerals decreases at the expense of hydrated forms of these minerals.

An interesting semiquantitative evaluation of the evolution of the mineral composition of bauxites with times is given by Bardossy [3], but he considered only "karst" bauxites.\* The distribution of Phanerozoic basic parageneses of the minerals of aluminum and iron is illustrated in Fig. 1 (some of the Phanerozoic data from Bardossy have been corrected by us).

It is easy to see that the pattern of change over time of the mineral composition of the karst bauxites (about 15% of the total world reserves [3]) are similar to these for all types of these ores [7]. The difference is only in the ratios of the contents of the different minerals (Fig. 2).

The second indisputable indication of a change in time of the conditions of bauxite formation is the pattern we have established of a change from the Paleozoic to the Cenozoic of

\*Bardossy includes in the group of karst bauxites all deposits overlying carbonate or mixed aluminosilicate-carbonate substrates.

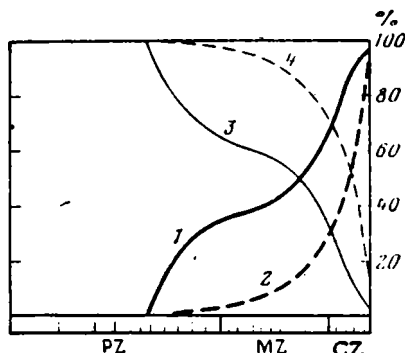


Fig. 2. Change in the contents of gibbsite and the total contents of boehmite, diaspore, and corundum (in percent of total content of these minerals) in bauxites in general and in karst bauxites. 1) Gibbsite in bauxites, overall; 2) gibbsite in karst bauxites; 3) boehmite, diaspore, and corundum in bauxites; 4) boehmite, diaspore, and corundum in karst bauxites.

the spectrum of parent rocks. In the Cenozoic these are primarily aluminosilicate rocks of the most varied composition (basic, intermediate, acidic). Deposits overlying carbonates are also known for this period (Yamaika, Pacific Ocean islands), but the number of such deposits and their reserves are less than a twentieth of the reserves of bauxite deposits not associated with carbonate rocks.

The situation in the Mesozoic and Cenozoic is completely different. Here bauxite deposits on an aluminosilicate substrate are an exception, and the "rule" is for deposits to be associated to some degree with carbonate rocks. It is also important to note that in contrast to the Cenozoic, for the Paleozoic a high degree of selectivity in terms of substrate composition is characteristic of the bauxite-formation processes. Of these changes with time we have established in the chemical composition of the bauxites and the parent-rock substrate are opposite in sign for 61.7% of the elements investigated; the others are not related by a strict correlational dependence [7]. From this it follows that the evolution of the bauxite-formation processes is caused by the change in the physicochemical parameters of the environment of bauxite-formation, and not the composition of the parent material.

The third sign of the change of bauxite-formation with time is the regular change of paleogeographic position of the bauxite-forming deposits from the Riphean to the Cenozoic, which has been clearly formulated by Mikhailov [12, 13], who noted that from the late Riphean to the Cenozoic there has occurred a regular shift of the optimal conditions of localization of bauxite deposits from coastal plains, lagoons, and oceanic shallows in the late Proterozoic to more elevated parts of the dry land in the late Cenozoic. Also most interesting is the areal relationship noted by Mikhailov of the distribution of pre-Mesozoic bauxite deposits with the coast line of the ocean basins and the lack, or weaker expression of this in the Cretaceous-Paleogene and especially the Oligocene-Quaternary epoch.

Finally, it seems to us that an evolutionary interpretation is entirely possible for the change with time of the scale of bauxite formation, in any event in the form in which this is reflected in the distribution of known reserves of bauxite deposits for the major periods of bauxite formation.

As is well known, conclusions about the distribution of bauxite ores with respect to the geological time scale are practically identical, even though the numerous publications devoted to the problem were written at different times with different aims by authors [3, 4, 8, 9, 12, 13, 15, 18, et al.], often holding entirely different views concerning the genesis of the deposits. This consensus view is as follows.

An absolute majority of bauxite deposits and 90-95% of the economic deposits of these ores are associated with the youngest period of bauxite formation. All other deposits account for only 5-10% of the bauxite reserves, which are essentially restricted to the late Proterozoic: the early Cambrian, the Devonian, the Carboniferous, the Triassic, the Jurassic, and the early Cretaceous, late Cretaceous, and Paleogene. Sequences older than the late Proterozoic do not contain economic bauxite deposits, even though there are numerous references in the literature to finds in the most ancient rock sequences, qualified as altered bauxites (emeries, diasporites, etc.).

The reason for the concentration of a large number of major bauxite deposits in the most recent strata is usually thought to be the incompleteness of this period of bauxite formation. It is assumed that in the future a great part of the bauxites will be destroyed by various processes of chemical and mechanical breakdown or burial, catagenesis, and metamorphism. However, in Africa, Australia, and South America a major part of the ores are far from pseudomor-

phic bauxites overlying the highs of positive relief forms, but rather crusts and pisolitic-oolitic varieties concentrated for the most part on the slopes at the foot of elevations. Many researchers think [1, 2] that these rocks can be considered characteristic representatives of deluvial, proluvial, alluvial, and, less commonly, coastal-basinal deposits. Furthermore, a significant number are already covered by nonbauxite rocks, i.e., they have been partially buried.

On the basis of the foregoing it must be conceded that the surprising productivity of the most recent period of bauxite formation is hardly due only to its incompleteness, but also depends on the specific features of the given period of development of the Earth that distinguish it from earlier periods.

One can likely account for the lack of bauxite deposits in the Precambrian using a similar approach. It is hardly justifiable to consider the reason for this as simply the result of the degradation of bauxites in the processes of catagenesis and metamorphism. Most likely it is related to the particular conditions existing on the Earth's surface during the most ancient times that prevented the broad development of bauxite-forming processes. Evidence in favor of this hypothesis is provided by the study of relatively young (Paleozoic, Mesozoic, Cenozoic) metamorphic sequences. Bauxite deposits metamorphosed to different degrees are known in Turkey, Iran, Afghanistan, Korea, China, Vietnam, the USSR, and a number of other countries. The bauxites of these deposits and the ore showings are truly strongly altered, being converted into diaspore and corundum rocks, partially schistose, cut by cracks, along which are developed such typically metamorphic minerals as margarite, chloritoid, micas, feldspars, pyroxenes, and amphiboles. However, despite such serious alterations, in the majority of cases these ores are reliably described as altered bauxites, and are not identified with diaspore- and corundum-containing formations of secondary quartzites, alunite zones, and other similar objects of endogenic or volcanogenic genesis.

Thus, analysis of published and new information shows that in the time from the Paleozoic to the Cenozoic, evolution of the mineral and chemical composition of bauxites is clearly manifested, the regular change of the original rocks from which they formed, the directed change of some characteristic features of the geological structure of the deposits, their paleogeographic and paleogeomorphic positions, and also the most intensive accumulation of these ores.

Strictly speaking, however, all other conditions being equal, the patterns found can be just as well interpreted as being the consequence of the evolution of the bauxite-forming processes themselves, and as the result of the action of superimposed processes (erosion, catagenesis, metamorphism) that transform originally identical ores after burial.

To solve this dilemma it is of interest to compare, on the one hand, the conditions of the catagenesis of bauxites of the same age, but located in different geological settings, and on the other hand, bauxites of different ages in similar geological situations.

Paleozoic bauxites have been reliably identified and satisfactorily studied in regions of the Northern and Southern Urals, Central and Southern Timan, the KMA, and the southeastern part of the Baltic Shield. It is not necessary to offer proof that the geological history of all these regions in the period after the burial of the Devonian or Carboniferous bauxites has differed considerably, since the composition of the underlying and overlying rocks is different. However, for all the Devonian bauxites of these areas the almost total absence of gibbsite and goethite is characteristic, and even though the minerals are present in Carboniferous bauxites they do not determine the general appearance of these ores, which are primarily boehmite and hematite. Furthermore, all Paleozoic bauxites contain significant amounts of chamosite as a rock-forming mineral, the presence of which has to be taken into account in developing technological schemes for their utilization.

For Mesozoic bauxites the picture is entirely different. For example, despite the fact that many deposits of these ores are covered by coaliferous or grey-colored sediments, chamosite is not widely distributed in them, and then only in zones of secondary bleaching. These ores differ substantially from those of the Paleozoic in the composition of the oxides and hydroxides of aluminum and iron, represented in general by gibbsite and goethite-hematite (in approximately equal amounts).

The bauxites being compared differ no less convincingly in their contaminant element concentrations. For example, all Paleozoic bauxites without exception differ so sharply from those of the Mesozoic in lithium content that this characteristic can successfully be used

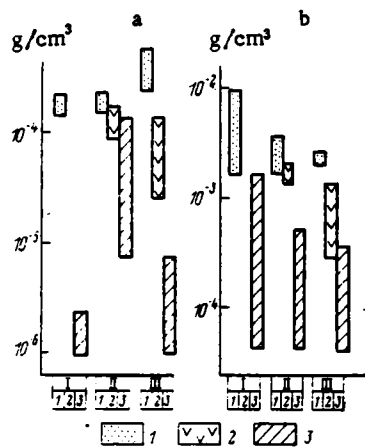


Fig. 3

Fig. 3. Range of changes in the mean (deposit) contents of lithium (a) and potassium (b) in bauxites of the Cenozoic (1), Mesozoic (2), and Paleozoic (3), differentiated by major genetic types of deposit [I) laterite; II) sedimentary-laterite in geosynclinal regions; III) the same, on platforms].

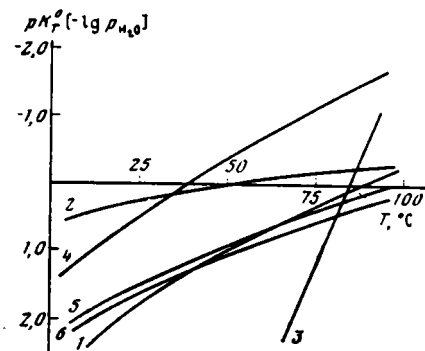


Fig. 4

Fig. 4. Variation of equilibrium constants of the following reactions with temperature: 1)  $\gamma\text{-Al}(\text{OH})_3 = \gamma\text{-AlO}(\text{OH}) + \text{H}_2\text{O}_g$ ; 2)  $\gamma\text{-Al}(\text{OH})_3 = \gamma\text{-AlO}(\text{OH}) + \text{H}_2\text{O}_l$ ; 3)  $\alpha\text{-FeO}(\text{OH}) = \frac{1}{2}\alpha\text{-Fe}_2\text{O}_3 + \frac{1}{2}\text{H}_2\text{O}_g$ ; 4)  $\alpha\text{-FeO}(\text{OH}) = \frac{1}{2}\alpha\text{-Fe}_2\text{O}_3 + \frac{1}{2}\text{H}_2\text{O}_l$ ; 5)  $\text{H}_2\text{O}_l = \text{H}_2\text{O}_g$ ; 6)  $\text{H}_2\text{O}_l = \text{H}_2\text{O}_g$  (at a relative humidity of 70%).

for dating these ores (Fig. 3). Similarly contrasted distributions in bauxites of different ages are exhibited by K, Co, Ni, Cu, Zn, Pb, Be, and TR.

Thus, despite the different history of the existence of bauxites of the same age after burial and sharply differing composition of rocks containing the ores, all deposits of the same or similar age are characterized by similar structural features and material composition. On comparing bauxites of different ages deposited under geologically similar conditions it is fairly easy to see marked differences in both their mineral and chemical compositions.

From here the conclusion naturally suggests itself that the basic reason for the picture presented of the evolution of the bauxite formation process and its mineralogical-geochemical embodiment/reification/manifestation are not the catagenic and metamorphic processes whereby these ores are transformed, but rather the regular change over time of the conditions of bauxite formation themselves that lead to the formation at different geological eras of bauxites of substantially different physical (mineral and chemical) composition.

A possible key to understanding the reason for this behavior is the analysis of the systems of gibbsite-water-boehmite and goethite-water-hematite, which can be described by the following chemical reactions:



For conditions of laterite weathering, the position of equilibrium clearly depends primarily on the temperature, and for reactions (1) and (3), on the partial pressure of water vapor as well ( $P_{\text{H}_2\text{O}}$ ).

The results of the corresponding calculations made using values of the constants from [14, 17] are shown in Figs. 4-6 and summarized in Table 1. The analysis of these materials allows us to make the following conclusions.

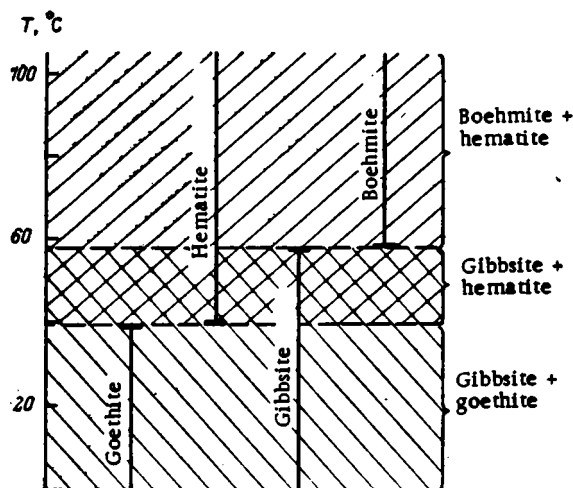


Fig. 5. Stability fields of the major parageneses of bauxites as a function of temperature in the presence of  $H_2O$ .

TABLE 1. Change in the Major Mineral Assemblages of the Oxides and Hydroxides of Aluminum and Iron as a Function of the Temperature of Bauxite Formation\*

| T °C  | Parageneses       |                   | Examples of typical deposits                                                                                                                            |
|-------|-------------------|-------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------|
|       | major             | secondary         |                                                                                                                                                         |
| <40   | Gibbsite-goethite | —                 | Eastern Ghats (India), Brazil, West Africa (pseudomorphic bauxites)                                                                                     |
| 40—58 | Gibbsite-hematite | Goethite          | Mesozoic deposits of Kazakhstan and Southern Mediterranean<br>Carboniferous deposits of Belgorod, Arkhangel'sk, and Leningrad Regions and the Komi ASSR |
| 58—66 | Boehmite-hematite | Gibbsite-goethite |                                                                                                                                                         |
| 66—83 | The same          | Goethite          |                                                                                                                                                         |
| >83   | ,                 | —                 | Devonian deposits of the Komi ASSR and the Northern and Southern Urals                                                                                  |

\* $P_{tot} = 1$  atm, relative humidity = 100%.

For a total atmospheric pressure of 1 atm and  $H_2O$ , in the system goethite-hematite and gibbsite-boehmite equilibrium is established at 40 and 58°C, respectively. Accordingly, in this case it is possible for the following three stable combinations to exist (cf. Figs. 4 and 5):

- 1) gibbsite-goethite at <40°C;
- 2) gibbsite-hematite at 40—58°C;
- 3) boehmite-hematite at >58°C.

Equilibrium in these same systems with  $H_2O$ \* is shifted to the region of higher temperatures and begins (at  $P_{tot} = 1$  atm, relative humidity of 100%) for the gibbsite-boehmite system at 66°C, and for the gibbsite-boehmite system at 83°C (cf. Figs. 4 and 6). Accordingly, the following parageneses can be expected to exist:

- 1) gibbsite-goethite at <66°C;
- 2) boehmite-goethite at 66—83°C;

\*Employing these conditions in the analysis of laterite weathering crusts is permissible since the bauxite zone is above the ground water level for more than 90% of the year [6, 11].

Since it is clear that in the bauxite zone of the laterite weathering profile the conditions of mineral formation are determined by the interaction of the solid phases with water in both the liquid and gaseous forms (depending on the season and the amount of precipitation) the mineral associates that form are more complex than indicated above (cf. Table 1).

The possibility of the formation and transition to the mineralized state of such nonequilibrium assemblages as gibbsite-hematite-goethite, boehmite-hematite-gibbsite-goethite, and boehmite-hematite-goethite is explained by the fact that thermodynamic conditions for equilibrium among gibbsite and boehmite, goethite, and hematite are considerably different for the formation process proper of these minerals and for the process of their interconversion, if these minerals have already formed. This is because an activation barrier of approximately 13-15 kJ/mole has to be overcome to dehydrate the already formed gibbsite or goethite, which shifts the equilibrium of the goethite- $\text{H}_2\text{O}$ -hematite system on the temperature scale to  $180-250^{\circ}\text{C}$ , and to  $220-300^{\circ}\text{C}$  for the gibbsite- $\text{H}_2\text{O}$ -boehmite system.

We shall explain this taking the conditions  $P_{\text{tot}} = 1 \text{ atm}$ ,  $T = 50^{\circ}\text{C}$  as an example.

Under these conditions in the dewatering period of the bauxite zone we are discussing in accordance with reactions (2) and (4) on the diagram in Fig. 4, the assemblage gibbsite-hematite must form. When the section dries out during the dry season or between rains, then in accordance with reactions (1) and (3) on the same diagram, gibbsite and hematite should form.

Thus, throughout the time of formation of the weathering profile, goethite will periodically form at some times, and hematite at others. At the same time the process must be quantitatively shifted in the direction of hematite formation, since this mineral forms under the conditions we are considering in the presence of  $\text{H}_2\text{O}$ , i.e., under the very conditions that result in the weathering, and goethite forms in the presence of  $\text{H}_2\text{O}$ , when only structural rearrangements of previously formed or forming amorphous phases of iron hydroxides can occur. Since the equilibrium of already formed goethite and hematite is determined ceteris paribus by higher temperatures, which are obviously not encountered in a weathering profile, the existence of these minerals and their transition to the mineralized state is completely justified thermodynamically.

An analogous situation must hold for the entire temperature interval from  $40$  to  $83^{\circ}\text{C}$  (cf. Table 1), the boundary temperature conditions within this interval for the appearance of the indicated assemblages being liable to change depending on the relative humidity. For example, for a relative humidity of 70%, the temperature limits for the formation of these parageneses will appear as follows:

- |                                        |                              |
|----------------------------------------|------------------------------|
| 1) gibbsite-hematite-goethite          | at $40-46^{\circ}\text{C}$ ; |
| 2) gibbsite-hematite-boehmite-goethite | at $46-58^{\circ}\text{C}$ ; |
| 3) boehmite-hematite-goethite          | at $58-81^{\circ}\text{C}$ ; |
| 4) boehmite-hematite                   | at $>81^{\circ}\text{C}$ .   |

From this it follows that all other conditions being the same, the formation of boehmite in laterite bauxites is more characteristic of conditions of when the dry seasons are more arid.

A more complex interrelation of the parageneses appears if we assume that the value of the total atmospheric pressure differed from that observed today (cf. Fig. 6). For example, for  $P_{\text{tot}} = 2 \text{ atm}$ , the limiting temperature parameters of the parageneses we are considering will have the following values (for a relative humidity of 100%):

- |                                        |                              |
|----------------------------------------|------------------------------|
| 1) gibbsite-goethite                   | at $<29^{\circ}\text{C}$ ;   |
| 2) gibbsite-hematite-goethite-boehmite | at $29-58^{\circ}\text{C}$ ; |
| 3) boehmite-hematite-goethite          | at $58-79^{\circ}\text{C}$ ; |
| 4) boehmite-hematite                   | at $>79^{\circ}\text{C}$ .   |

However, despite the obvious complexity of the dependence of the composition of the parageneses of the oxides and hydroxides of aluminum and iron on the change in temperature and at-



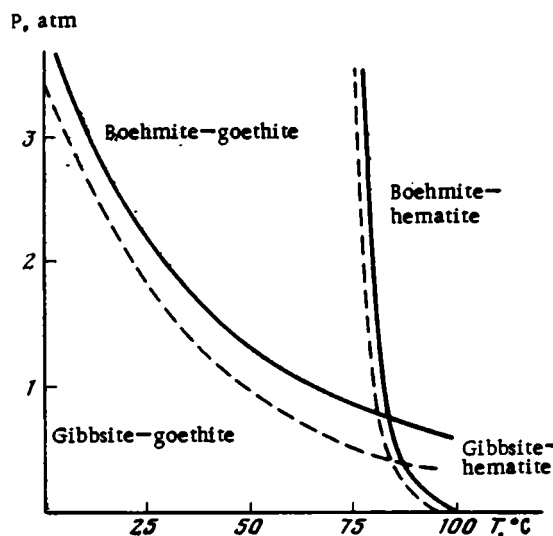


Fig. 6. Stability fields for major parageneses of bauxites in coordinates of P and T in the presence of  $H_2O$ . (Solid lines, relative humidity 100%; dashed lines, 70%).

mospheric pressure, a clear pattern appears that can be formulated as follows: the higher the temperature and the total pressure in the weathering zone, the greater the extent to which the gibbsite-goethite assemblage will be replaced by the boehmite-hematite assemblage, all other conditions being the same. The change in these assemblages agrees completely (at least in terms of temperature) with current ideas about the allowable level of PT conditions on the surface of the Earth ( $T \leq 100^\circ C$ ,  $P \sim 1$  atm). If this is so, then it is quite logical to assume (even if only as an hypothesis) that the change in time from the Paleozoic to the Cenozoic of the composition of bauxites found empirically [3, 7, 10, 16, et al.] is related to the decrease in the mean temperature on the surface of the Earth, at least in regions of bauxite formation.

In connection with this it is not difficult to estimate the PT conditions at the Earth's surface for the Phanerozoic (Fig. 7). As follows from this assessment, the temperature conditions in the weathering zone from the Paleozoic to the Cenozoic have changed over a wide range, from 20 to  $90^\circ C$  (constant P), the sharpest changes apparently being at the Devonian-Carboniferous boundary, the Late Cretaceous and Pliocene-Quaternary period. Without claiming absolute accuracy of the temperature values given (because of possible errors in the determination of the constants used, deviations of the actual compositions and structures of the minerals from those used in the evaluation, the unaccounted for effect of the true composition of the weathering solutions, etc.) it should be noted, however, that the pattern found cannot be ignored in assessing the bauxite formation in different geological eras.

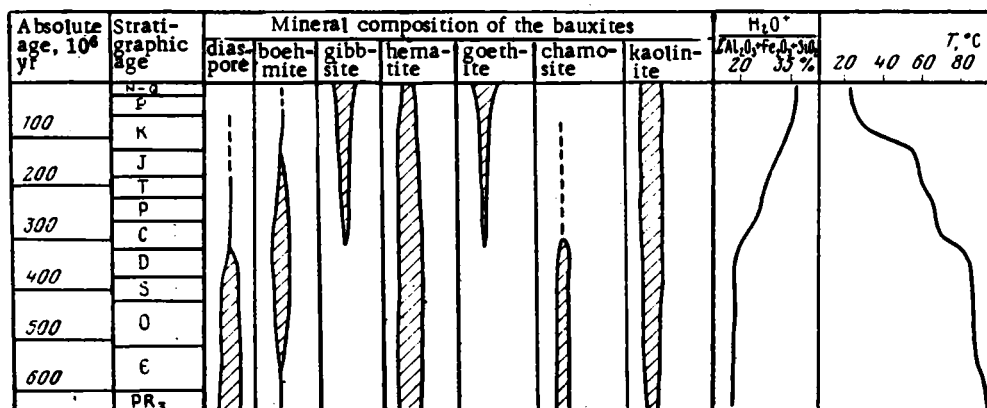


Fig. 7. Estimation of the minimal temperature of laterite bauxite formation (based on the thermodynamic analysis of the equilibrium composition of the major minerals of the bauxite paragenesis).

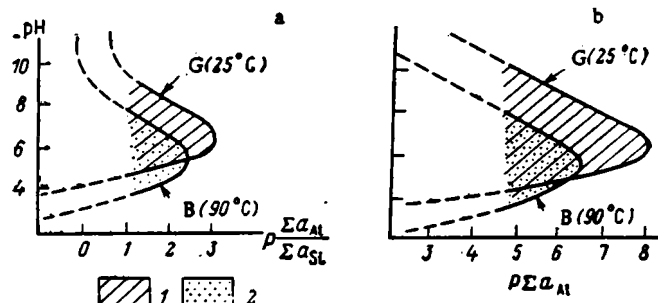


Fig. 8. Limiting values of  $\Sigma a_{Al}/\Sigma a_{Si}$  (a) and  $\Sigma a_{Al}$  (b) for bauxite formation as functions of solution pH. Shaded areas represent variations in the values observed in nature and experiments that permit the formation of gibbsite (1) and boehmite (2) bauxites.

The change from the Paleozoic to the Cenozoic of the boehmite-hematite to the gibbsite-goethite paragenesis as the temperature in the weathering sphere decreased entailed a substantial change in the concentration parameters of the ore-forming solutions in the laterite weathering profiles [6], for example, for bauxite and gibbsite formation at 90 and 25°C, respectively. At the same time the equilibrium concentrations of aluminum, iron, and silicon declined sharply, and the range of permissible pH variations and the concentration ratios of Al and Si for bauxite formations increased.

A consequence of these changes was the radical transformation of the conditions of bauxite formation and of a number of important properties of weathering products in the period when the Mesozoic and especially the younger laterite profiles were being formed. During lateritic bauxite formation in these times: the role of amorphous phases declined in the formation of the bauxite minerals; the degree of crystallization of the minerals being formed and their rate of formation increased; the sorptional capacity of the newly formed mineral phases was sharply reduced, which led to a decrease in the overall concentration of the contaminant elements in the bauxite material; the range of rocks from which bauxites could form expanded significantly, chiefly from rocks with high contents of alkali and alkali-earth elements, and also silicon.

The expansion of the "omnivorous" nature of the bauxite formation process led to the rise in the extensiveness of bauxite formation and correspondingly to an increase in the reserves of these ores.

Thus, it seems possible to us not only to represent the evolution of the substance of bauxites during Phanerozoic time relatively completely, but also to understand and formulate the causes and "mechanisms" that give rise to, control, and assure this evolution.

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# FEATURES OF STRUCTURE AND COMPOSITION OF THE LOWER CARBONIFEROUS MANGANESE DEPOSITS IN SOUTH URAL

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UDC 553.32:551.735(574.11)

The structure and composition of the manganese deposits in the Zianchura ore field are described. New data are given on the distribution of the mineralization in the enclosing rocks and the chemical and mineral composition of oxidized manganese ores. The manganese accumulation mechanism in gaizelike silicites is described.

Lower Carboniferous deposits are widespread on the western slope of South Ural, where they are traceable as a narrow meridional strip within the linear folded zone along the western boundary of the Zilair synclinorium.

In the region under study these deposits belong to the carbonate-terrigenous-silicic manganese formation, associated with numerous ore shows and minor manganese deposits, described in the literature under the common name of the Zianchura deposit [1]. The distinctive features of this formation are its exclusive Visean age and the widespread manganese metallization observed in silicic-clay rocks over a stretch of up to 100 km.

The manganese metallization of the Lower Carboniferous in the Zianchura ore field was studied during World War II [1] and in the last decade.

Until now, however, the commercial prospects of manganese in this area has remained unclear because of the lack of data on the distribution of the metallization in the enclosing rock and the mineral composition of the manganese ores in the oxidation zone and in the deep interior.

The studies of the Lower Carboniferous manganese deposits of the Zianchura region by the author in 1981-84 revealed features of the structures and composition of ore formations and also, to a large extent, the mechanism of manganese accumulation.

## GENERAL CHARACTERISTICS OF MANGANESE DEPOSITS

Most manganese ore shows of the western slope of the South Ural are concentrated in the Zianchura area. They are all associated with the Lower Carboniferous rocks traced as a continuous strip, 6-15 km wide, for tens of kilometers from north to south — from the latitudinal current of the Bolshoi Ik River to the Akberdy River.

In the Lower Carboniferous of this area, Tournaisian, Visean, and Namurian stages are identified. The Tournaisian stage is represented by two suites. The lower — Yamashla — suite consists of silicites and limestones with minor argillite interlayers. The rhythmic alternation of rocks of different compositions endows the Yamashla suite with a flysch-like appearance. The thickness varies along the course from north to south between 150 and 350 m. The upper portion of the Tournaisian stage is formed by the Mazitov suite, which occurs with a gradual transition into the Yamashla suite. In its profile, argillites are predominant, with a lesser presence of sandstones and rare limestone interlayers. The suite in the northern part of the region is 120-190 m thick, expanding up to 500 m in the southerly direction.

In the Visean stage, Kuruil and Itkulov suites are seen distinctly, as is the lower portion of the Bukharcha suite.

At the bottom, the Kuruil suite is formed of interstratified (layers of 0.3-2 m) limestone, argillite, and silicite. The former two are present in approximately equal proportions in each member, with silicite playing a secondary role. According to studies in

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TABLE 1. Results of Microsilicate Spectrum Analysis of Ore-Free Clay-Silicic Rocks, Seregulov Horizon, %

| Rock                        | SiO <sub>2</sub> | Al <sub>2</sub> O <sub>3</sub> | Fe <sub>2</sub> O <sub>3</sub> | TiO <sub>2</sub> | CaO  | MgO  | MnO <sub>2</sub> |
|-----------------------------|------------------|--------------------------------|--------------------------------|------------------|------|------|------------------|
| Brownish-yellowish silicite | 85,8             | 3,10                           | 6,20                           | 0,12             | 0,35 | 0,55 | 0,16             |
|                             | 81,1             | 6,80                           | 8,30                           | 0,18             | 0,90 | 1,0  | 0,12             |
| Light-gray silicite         | 88,0             | 4,20                           | 2,30                           | 0,13             | 0,30 | 0,80 | 0,14             |
|                             | 87,0             | 4,0                            | 2,50                           | 0,14             | 0,40 | 0,80 | 0,08             |
|                             | 85,2             | 6,70                           | 2,90                           | 0,15             | 0,90 | 0,90 | 0,10             |
|                             | 85,5             | 4,10                           | 2,80                           | 0,16             | 0,40 | 0,80 | 0,14             |
| Mean                        | 84,1             | 4,80                           | 4,20                           | 0,15             | 0,55 | 0,80 | 0,12             |

1974-77 by Makushin, a manganese ore (Seregulov) horizon can be identified at the bottom of Kuruil suite; it consists of rhythmically interstratified silicified limestone, silicic argillite, and gaizelike silicite, with a predominance of the latter. The manganese metallization is concentrated mainly in gaizelike rocks and less in limestone. The width of the Seregulov ore horizon outcrops varies from 10 to 40 m.

The upper portion of the Kuruil suite consists of limestone with thin (0.1-1.5 m) argillite and silicite interlayers. The suite gradually grows in thickness north to south from 110 to 300 m. In the southern part of the region, limestone is completely replaced by sandstone and argillite.

The Itkulov suite overlies Kuruil rocks conformally with a gradual transition. Argillites are predominant in the profile and are interstratified with thin (0.1-0.3 m) interlayers and medium (2-5 m) members of limestone and silicite. Southward the amount of sand and calcareous material gradually increases in clay rocks. Sporadic iron-manganese accumulations forming small ore bodies are documented in the interlayers (0.2-1 m) of gaizelike silicite throughout the profile of the Itkulov suite, traceable over distances of up to 200 m. Due to the iron concentration and limited occurrence in plan, these ores are of no commercial interest. Heavily calcareous polymict sandstone also occurs frequently in the Itkulov suite, with iron and manganese hydroxides observable along broken edges of cracks. The total thickness of the Itkulov suite varies along the course from north to south between 135 and 500 m.

The Bukharcha suite encompasses Visean and Namurian sediments, which have no distinct boundary. The suite consists mainly of limestone, which forms two members with different structure and other features, unequal in thickness. The lower member is formed of stratified silicic organogenic limestone with rare silicite and sandstone interlayers; its thickness does not exceed 80 m. The upper member consists of thick-layered bituminous limestone, with thin silicon lenses; its thickness is up to 270 m. The limestone of the lower member belongs to the Upper Visean and that of the lower member to the Namurian.

Numerous longitudinal overthrusts are observed in this area, which divide the sedimentary formations into separate tectonic shells, thrust in succession, one upon the other, from the east [2] and brought so close together that only their frontal zones are exposed.

The Lower Carboniferous manganese sediments form anticlines developed along the frontal parts of these shells. They are intensely dislocated and exhibit steep occurrence at angles of 50-70°, which is locally vertical or even overturned. The anticlines are extremely long, stretching for tens of kilometers, with a width of just 1-4 km. The anticline zones have an asymmetrical structure. Their western flanks are usually steeper than their eastern flanks. The joints of linear structures dip southward gently (fractions of a degree).

Kazantsev [2] has identified on Zianchura territory the Verkhnebikberda and Bogdanov anticlines, with Lower Carboniferous manganese sediments exposed in the cores of each.

#### STRUCTURAL FEATURES AND COMPOSITION OF THE SEREGULOV ORE HORIZON

The Seregulov manganese ore horizon can be traced over more than 80 km. Its main structural feature is a rhythmic interstratification of different clay, carbonate, and silicic rocks, with an uneven distribution of manganese metallization.

The Seregulov horizon often exhibits argillite interlayers (0.2-1 m) of a greenish-gray, dark-green, or olive-green color. These are usually finely foliated or tabellar, less often

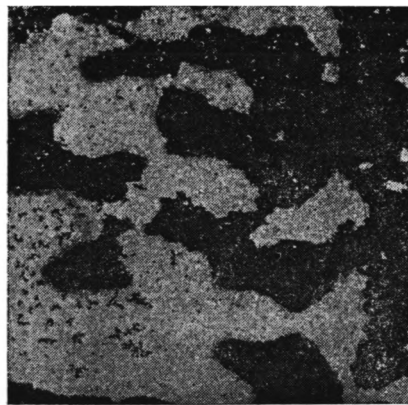


Fig. 1

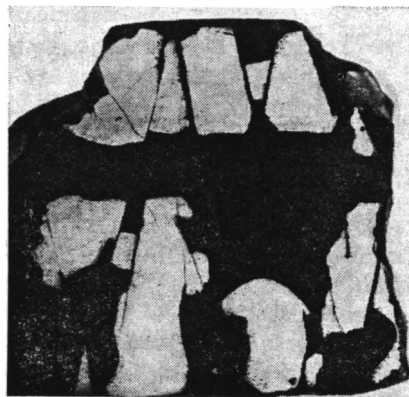


Fig. 2



Fig. 3

Fig. 1. Manganese hydroxides replacing gaizelike silicites (polished section 34,  $\times 5$ , single nicol).

Fig. 2. Relict portions of gaizelike silicites in the ore mass (specimen 69, actual size).

Fig. 3. Cracks in gaizelike silicites filled with manganese hydroxides (polished section 86,  $\times 6$ , single nicol).

lumpy varieties with a cavernous broken surface and greasy to the touch. By composition, argillites are subdivided into silicic, chloritic, micaceous, calcareous-silicic, and mica-ceous-silicic. Manganese oxide contents in argillites vary from 0.4 to 0.8%, with a mean of 0.55%.

The carbonate rocks of the Seregulov horizon are more important than the clay rocks. They consist of thin (0.2-1 m) limestone layers of two types. The first, more frequent, layer is formed of massive thin- and thick-plated pelitomorphous, dark-gray, less often gray, limestone, with various silicic contents. The second type is dark spongy, fine-detrital silicified limestone. Small (up to 2 mm) nests and thin (0.2-0.5 mm) manganese ore cross-veinlets are frequent in the carbonate rocks. They are usually more common in fine detrital limestone than in pelitomorphous varieties, due to their different lithologic compositions. The former are more intensely silified and enriched in ore components. Manganese oxide content in them ranges from 6.2 to 7.80%, with a mean of 7%, while in pelitomorphous limestone it does not exceed an average of 2.1%.

Clay-silicic rocks are most important in the productive horizon; they are represented by numerous interlayers of gaizelike silicite (0.2-2 m), in which the bulk of manganese compounds are localized. They usually occur conformably with the enclosing limestone and argillite and are distinctly marked in the cross section by variegated pigmentation and fine-tabellar structure.

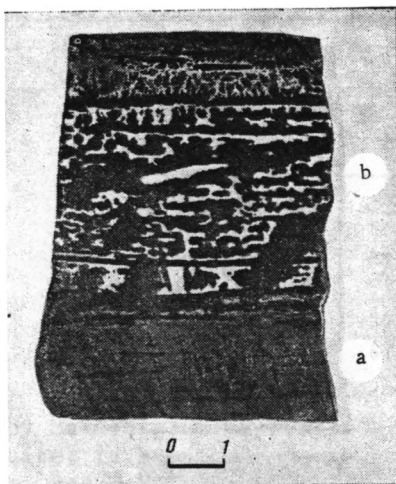


Fig. 4

Fig. 4. Uneven distribution of manganese metallization at the contact zone of limestones (a) and silicites (b); specimen 96.

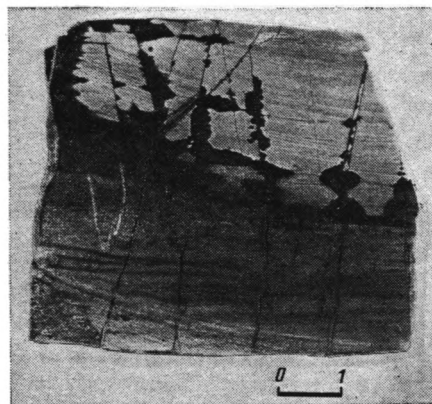


Fig. 5

Fig. 5. Distribution of manganese hydroxides at the contact of limestone (a) and silicite (b); specimen 89.

Gaizelike silicite is a silicic microporous olive brown-yellow (to off-white) rock composed of silica (chalcedony), with an admixture of quartz and finely dispersed clay matter. These rocks exhibit a diversity of structure and are substituted by manganese hydroxides to different degrees. Even within isolated ore interlayers manganese compounds are distributed unevenly: while in some they replace the groundmass of gaizelike silicite almost completely, in others they only replace a small portion of it.

The nonmetalliferous gaizelike silicites contain a large proportion of silica and an extremely low amount of manganese (Table 1).

The principal rock-forming minerals are chalcedony and quartz, with minor amounts of montmorillonite, hydromica, kaolinite, chlorite, calcite, and goethite.

In the Seregulov horizon, manganese metallization is represented by two morphologic types. The first type consists of fine veinlets and thin layers (0.5-1.0 cm, less often 3-5 cm) of manganese compounds. Usually, they fill small cracks in gaizelike silicites. The second type consists of manganese hydroxides, permeating and replacing finely dispersed clay-silicic mass of gaizelike rocks (Fig. 1). The relict portions of enclosing rocks left intact by the substitution appear immersed in the ore mass (Fig. 2), which often etches their perimeters and penetrates inside the gaizelike silicite.

The degree of replacement of these enclosing rocks by ore matter depends on the rock structure. In heavily porous silicites, clay silicic mass is usually replaced to the greatest degree, while in low-porosity varieties the substitution is minimal. Cracks in the rocks also play a role, as manganese compounds leak through them into gaizelike silicite and permeate it (Fig. 3).

Ore aggregates of two types are formed by substitution of manganese hydroxides for the parent rocks. The first type are ores with a cement structure, largely repeating structural and textural features of gaizelike silicites. The selectivity of the manganese ore process often emphasizes the structural pattern and the texture of gaizelike rocks, making them more visible. The second type is infrequent; it is characterized by metasomatic development of stemlike crystal aggregates and pisolite segregations up to 0.5 cm, occurring on the stratification planes of clay-silicic rocks.

It is a characteristic feature of manganese metallization that it is confined mainly to gaizelike silicites. The contacts of silicite with limestone are often emphasized by a sharp boundary of manganese hydroxide occurrence, attributable to the different permeabilities of the two rocks (Fig. 4). Even when cracks cut across limestone and silicite in the near-contact zone, manganese metallization is localized in clay-silicic mass of the latter (Fig. 5).

TABLE 2. Chemical Composition of Clay-Silicic Manganese Ores, Seregulov Horizon, %

| Rock                          | SiO <sub>2</sub> | Al <sub>2</sub> O <sub>3</sub> | Fe <sub>2</sub> O <sub>3</sub> | TiO <sub>2</sub> | CaO  | MgO  | MnO <sub>2</sub> | Na <sub>2</sub> O | K <sub>2</sub> O | Loss to annealing | Total  |
|-------------------------------|------------------|--------------------------------|--------------------------------|------------------|------|------|------------------|-------------------|------------------|-------------------|--------|
| Gaizelike silicite            | 60,0             | 5,10                           | 6,50                           | 0,20             | 4,00 | 3,60 | 13,4             | 0,16              | 0,40             | 6,70              | 100,06 |
|                               | 55,8             | 4,80                           | 6,20                           | 0,20             | 4,60 | 2,30 | 19,4             | 0,16              | 0,40             | 6,20              | 99,86  |
|                               | 59,0             | 5,50                           | 4,70                           | 0,40             | 4,30 | 3,50 | 14,3             | 0,14              | 0,70             | 7,10              | 99,64  |
|                               | 60,8             | 4,70                           | 5,00                           | 0,25             | 4,60 | 1,25 | 15,2             | 0,16              | 0,50             | 7,20              | 99,66  |
|                               | 60,5             | 4,40                           | 6,40                           | 0,10             | 4,50 | 0,60 | 17,2             | 0,14              | 0,40             | 5,50              | 99,74  |
|                               | 62,5             | 2,40                           | 6,60                           | 0,10             | 4,50 | 0,70 | 17,2             | 0,14              | 0,40             | 5,40              | 99,94  |
|                               | 59,0             | 4,80                           | 3,80                           | 0,10             | 3,80 | 0,80 | 20,5             | 0,10              | 0,60             | 6,50              | 100,0  |
| Mean                          | 59,7             | 4,50                           | 5,60                           | 0,20             | 4,30 | 1,80 | 16,7             | 0,14              | 0,50             | 6,40              | 99,84  |
| Gaizelike calcareous silicite | 47,5             | 4,20                           | 2,90                           | 0,20             | 14,2 | 0,30 | 18,5             | 0,14              | 0,60             | 11,2              | 99,74  |
|                               | 53,6             | 5,50                           | 5,60                           | 0,30             | 10,0 | 1,80 | 13,0             | 0,14              | 0,60             | 7,40              | 99,94  |
|                               | 49,9             | 4,60                           | 4,50                           | 0,20             | 10,7 | 2,00 | 16,2             | 0,14              | 0,50             | 11,0              | 99,74  |
| Mean                          | 51,0             | 4,80                           | 4,30                           | 0,26             | 11,6 | 1,40 | 15,9             | 0,14              | 0,56             | 9,90              | 99,86  |

Metalliferous gaizelike silicites differ from ore varieties in chemical composition. They have a much lower silica content, a sharply higher concentration of manganese compounds, and a heightened carbonate content (Table 2).

By x-ray structural investigations, gaizelike manganese rocks of the Seregulov horizon consist mainly of quartz (chalcedony), kaolinite, and calcite.

#### AREA DISTRIBUTION OF MANGANESE METALLIZATION

Seregulov manganese deposits can be traced almost everywhere along the course in the axial parts of anticlinal folds within the ore field over tens of kilometers. A detailed study of the profiles of the metalliferous horizon at different sites has shown that the intensity of manganese mineralization of gaizelike rocks correlates directly with the degree of rock alteration. In the southern part of the ore field, for example, manganese silicite displays substantial silicification and brownish-yellow color due to a higher iron hydroxide content. Manganese concentration in these rocks is not usually high (from 8 to 21.5%). Substitution of ore for rocks in this area is not intense.

To the north, at the center of the area, light-gray (decolored) silicites often occur in the profile of metalliferous horizon, as well as brownish-yellow magnanized silicite. Silica and iron contents are lower in the former than in the brownish-yellow varieties, while manganese hydroxide content rises to 35%. In the northern part of the area Seregulov layers exhibit a predominance of light (offwhite) manganese silicite over brownish-yellow varieties; the manganese content in ore formations of decolored silicites rises to 60%, while the amount of silica drops by almost two times compared with brownish-yellow varieties. The maximum manganese mineralization and depigmentation of gaizelike silicite is usually focused in the intervals of an ore horizon, where disjunctive faults are present.

In the northern part of the territory the intensity of ore substitution for country rocks is most pronounced, probably because of a proximity to the source of manganese solutions. According to our conjecture, this source was located north of the area, near the Muradymov fault, which stretches latitudinally along the Bolshoi Ik River.

#### BRIEF DESCRIPTION OF MANGANESE ORES

The structural and textural features of manganese ores described above are generally representative of their superimposed nature. These ores have experienced hypergenetic alterations, largely camouflaging the primary nature of manganese units and ultimately determining their chemical and mineral composition.

We have selected and investigated cores of manganese ores uncovered by trenches at various sites in the Zianchura ore field. The composition of the Seregulov manganese ores is described by the data in Table 3, which shows that the ore accumulations located in brownish-yellow gaizelike silicites differ in the contents of the principal components from those from light-gray (decolored) silicites.

In particular, the ore from brownish-yellow silicite has twice as much silica and twice as little manganese as the ores from decolored gaizelike rocks due to the stronger influence of metalliferous solutions on the latter type.



TABLE 3. Chemical Composition of Manganese Ores, Seregulov Horizon

| Component                      | Manganese ores in brownish-yellowish silicite |       |        |       |        |        |       |       | Mean | Manganese ores in brownish-yellowish silicite |       |       |       |       |       |       |  | Mean |
|--------------------------------|-----------------------------------------------|-------|--------|-------|--------|--------|-------|-------|------|-----------------------------------------------|-------|-------|-------|-------|-------|-------|--|------|
| SiO <sub>2</sub>               | 59,0                                          | 60,0  | 46,3   | 50,5  | 57,3   | 57,5   | 55,2  | 55,1  |      | 26,6                                          | 32,1  | 20,1  | 39,4  | 21,2  | 29,8  | 28,2  |  |      |
| Al <sub>2</sub> O <sub>3</sub> | 4,80                                          | 3,50  | 2,50   | 3,20  | 2,60   | 3,20   | 2,30  | 3,16  |      | 2,60                                          | 2,30  | 1,90  | 2,50  | 0,90  | 2,90  | 2,18  |  |      |
| Fe <sub>2</sub> O <sub>3</sub> | 3,86                                          | 2,80  | 3,00   | 4,20  | 3,50   | 4,52   | 4,80  | 3,80  |      | 2,90                                          | 2,50  | 4,60  | 5,20  | 3,64  | 3,20  | 3,67  |  |      |
| TiO <sub>2</sub>               | 0,13                                          | 0,10  | 0,08   | 0,10  | 0,08   | 0,05   | 0,06  | 0,08  |      | 0,10                                          | 0,07  | 0,08  | 0,09  | 0,06  | 0,08  | 0,08  |  |      |
| CaO                            | 3,65                                          | 1,40  | 3,20   | 2,90  | 2,00   | 2,00   | 3,00  | 2,62  |      | 3,50                                          | 1,70  | 2,60  | 2,00  | 2,70  | 2,60  | 2,54  |  |      |
| MgO                            | 0,87                                          | 1,10  | 1,30   | 1,50  | 1,10   | 0,80   | 1,00  | 1,10  |      | 1,20                                          | 1,20  | 1,90  | 2,00  | 1,10  | 2,40  | 1,65  |  |      |
| MnO                            | 2,40                                          | 3,40  | 4,40   | 2,50  | 3,20   | 2,90   | 2,30  | 3,00  |      | 14,0                                          | 5,60  | 7,60  | 4,40  | 6,30  | 5,60  | 7,28  |  |      |
| MnO <sub>2</sub>               | 18,1                                          | 21,2  | 30,6   | 28,2  | 23,3   | 21,6   | 23,1  | 23,4  |      | 38,8                                          | 45,7  | 48,6  | 34,0  | 53,6  | 41,3  | 43,7  |  |      |
| P <sub>2</sub> O <sub>5</sub>  | 0,08                                          | 0,06  | 0,08   | 0,20  | 0,10   | 0,12   | 0,10  | 0,11  |      | 0,08                                          | 0,09  | 0,10  | 0,09  | 0,08  | 0,09  | 0,09  |  |      |
| Na <sub>2</sub> O              | 0,12                                          | 0,20  | 0,15   | 0,15  | 0,15   | 0,15   | 0,12  | 0,15  |      | 0,30                                          | 0,30  | 0,40  | 0,30  | 0,30  | 0,30  | 0,32  |  |      |
| K <sub>2</sub> O               | 0,50                                          | 0,40  | 0,30   | 0,20  | 0,20   | 0,20   | 0,20  | 0,30  |      | 0,50                                          | 0,40  | 0,40  | 0,30  | 0,30  | 0,30  | 0,37  |  |      |
| Loss to annealing              | 6,30                                          | 5,80  | 8,10   | 8,30  | 6,50   | 7,00   | 7,80  | 7,16  |      | 9,20                                          | 8,00  | 11,7  | 9,40  | 9,40  | 11,3  | 9,83  |  |      |
| Total                          | 100,01                                        | 99,96 | 100,01 | 99,95 | 100,01 | 100,04 | 99,98 | 99,98 |      | 99,78                                         | 99,96 | 99,96 | 99,68 | 99,58 | 99,87 | 99,91 |  |      |

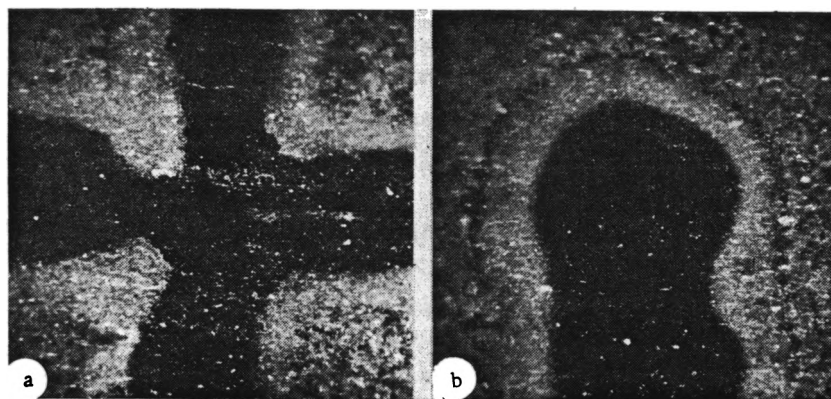


Fig. 6. Decolored portions of brownish-yellow silicite near cracks (a) and apophyses (b) with manganese mineralization (polished section 57,  $\times 20$ , single nicol).

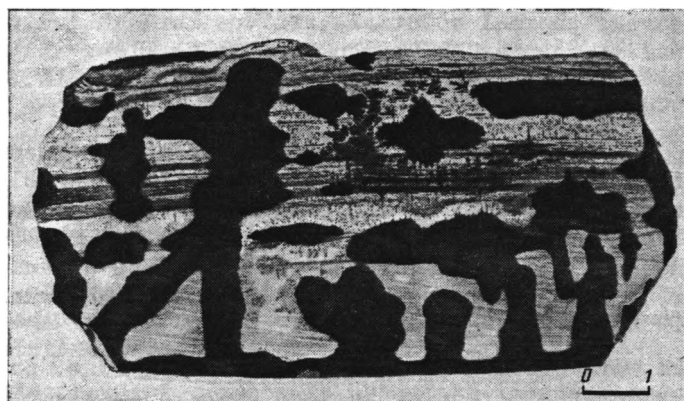


Fig. 7. Decolored silicite with manganese metalization; specimen 86.

By chemical data, oxidized Seregulov variety is a silicic-manganese ore with a minor admixture of carbonate iron (siderite) and low sulfur and phosphorus contents.

Detailed minerographic studies of the manganese ores have identified the presence of the following minerals: todorokite, psilomelane (cryptomelane), rancieite, vernadite, pyrolusite, goethite, and hematite, which reflect the influence of the various processes on manganese metallization.

The principal ore-forming minerals are todorokite, cryptomelane, and rancieite, less often pyrolusite and in single instance vernadite.

The minerals are distributed unevenly across the Zianchura ore field. At the center of the field todorokite and cryptomelane are predominant, with some presence of goethite, while in the northern part todorokite and rancieite are the main minerals. The mineral composition of Seregulov ores shows that they are uniform and belong to hypergenesis zones.

#### · ORIGINS OF MANGANESE ORES

The origins of manganese ores in the Lower Carboniferous of the Zianchura region has been variously explained by different investigators. For example, Betekhtin [1] assumes that manganese ore accumulated mainly in the littoral zone of a marine basin. Accordingly, he interpreted the manganese ore of the Zianchura ore field as a sedimentary entity. Other investigators have classified the manganese metallization of the Seregulov horizon as an exhalation-sedimentary sedimentation-diagenetic unit.

The new data reported here shed some light on the formation mechanism of manganese ores in the Lower Carboniferous of the Zianchura area. It should be stressed that the

objects in question are situated in the hypergenesis zone and have experienced intense weathering and oxidation, largely obscuring their primary nature.

Nevertheless, the available data warrant several conclusions:

- the manganese metallization within the Zianchura ore field is of a superimposed nature;
- the ore entities of the Seregulov horizon have developed by metasomatic substitution of previously formed clay-silicic rocks by manganese oxides and hydroxides; and
- manganese compounds were brought into gaizelike silicites by thermal solutions which penetrated through cracks and permeated a porous groundmass.

Brownish-yellow heavily silicified silicites often show traces of penetration of manganese solutions through crossing cracks and apophyses (Fig. 6). The country rocks near these cracks are lightened, due to the action of mineralized solutions.

Gaizelike silicites, which were less silicified and heavily porous, were affected more by the thermal metalliferous solutions, resulting in their total decoloring and maximum replacement by manganese hydroxides (Fig. 7).

We believe that manganese thermal solutions arrived through faults from deeper horizons into the core of anticlinal structures and circulated there along disjunctive faults. Manganese ores were formed as a result of the discharge of thermal solutions in gaizelike silicites.

We thus hypothesized the existence of an endogenous source of manganese metallization, probably in the area of the Muradymov fault. It does not seem possible at the moment to define the genesis of the manganese ores of the Seregulov horizon or evaluate their commercial quality, since no bore holes have been drilled in the Zianchura ore field. The primary origin of the manganese in these ores cannot be determined definitively at this point. Our data suggest, however, that manganese in silicite was originally accumulated during the process of sedimentation.

Later, when the rocks were brought into the hypergenesis zone, ore matter was transported into gaizelike rocks of the Seregulov horizon by circulating thermal solutions, mobilizing manganese from underlying rocks with disseminated manganese compounds and from ore bodies in deeper horizons; finally, manganese could also arrive from a plutonic source.

Definitive answers to these questions will not be obtained before drilling of holes to uncover the primary manganese ores of the Lower Carboniferous beneath the hypergenesis zone and determine their genetic types and commercial value.

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GEOLOGICAL-GEOCHEMICAL PRECONDITIONS OF MANGANESE ORE  
FORMATION, MANGYSHLAK DEPOSIT.  
PART I. GEOLOGY OF THE DEPOSIT

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UDC 553.32(574)

A detailed discussion of the geological makeup of the Mangyshlak deposit is given, including its sedimentary sequence, the compositional and structural features of the productive unit and of the enclosed ores. Geological and geochemical indications are that only the carbonate ores are primary. For the first time, kariolite formation processes are described. Kariolites develop through oxidation of the carbonate ore.

The formation conditions of Oligocene-age manganese ores in the southern USSR have always been of great interest to geologists, but this remained an unresolved issue. Opinions differ on the genesis of the Mangyshlak deposit. Attention was focused on a single deposit and the following: all Oligocene deposits carry numerous similar characteristics and this suggests that characteristics found in individual deposits may also be valid for the rest; that they are of uniform validity.

Assumptions about the genetic conditions of the Mangyshlak ore deposits are varied. Opinions differ primarily on the source of the ore matter. Some workers derived it from the weathering horizons, others related ores to volcanism. Thus a "normal"-sedimentary and volcanic(hydrothermal)-sedimentary theory evolved. A more detailed discussion of the genetic concepts follows a descriptive part.

A large body of geological information is needed to resolve the genetic question. These include not only data on the deposit itself but also its general geological setting and characteristics of the sediments that enclose the ores; both those that include ore bodies and those found beyond the producing ores. By using such a complex approach, the origin of the ore matter and the formation conditions of the deposit may be resolved. These are the essential problems facing researchers.

The Mangyshlak deposit occurs in the lower part of the Maikop Series (Oligocene-Lower Miocene) among Middle Oligocene (Kuyulussk Formation) deposits. The Series is composed of a terrigenous complex, mostly clayey rocks, underlain by Eocene marls. A gradual transition exists between the carbonate and terrigenous sediments, although it occurs fast, through a limey clay unit. The higher horizons of the Maikop Series had been eroded. Judging from its remnants, it seems that the original thickness exceeded 800 m.

The Oligocene basin was inherited from earlier times. However, it carries characteristics that distinguish it from the Eocene basin. Subsidence sharply increased in early Oligocene times and this caused a distinct differentiation in the basin bottom morphology. Marginal shelf zones evolved and deep basinal zones, the subsidence of which was not compensated by sediment accumulation [9, 12, 13, 17, 18]. In addition to the evolution of these basins (Fig. 1, VII and IX), individual basement blocks were uplifted. An island developed at the same time in the present Karatau Ridge area (Fig. 1, II). At lower levels, sediments formed only in the inner shelf zone of the Oligocene basin occur. The Mangyshlak deposit is associated with these. This zone stretches along the southern slope of the Karatau Range, surrounds the Chakyransk syncline, and extends northwestward, toward the Tyubkaragan Peninsula.

West of the Tyubkaragan, the Oligocene sequence occurs in its entire thickness (Fig. 1, Location 1). In the eastern part of the peninsula the highest Oligocene horizons are over-

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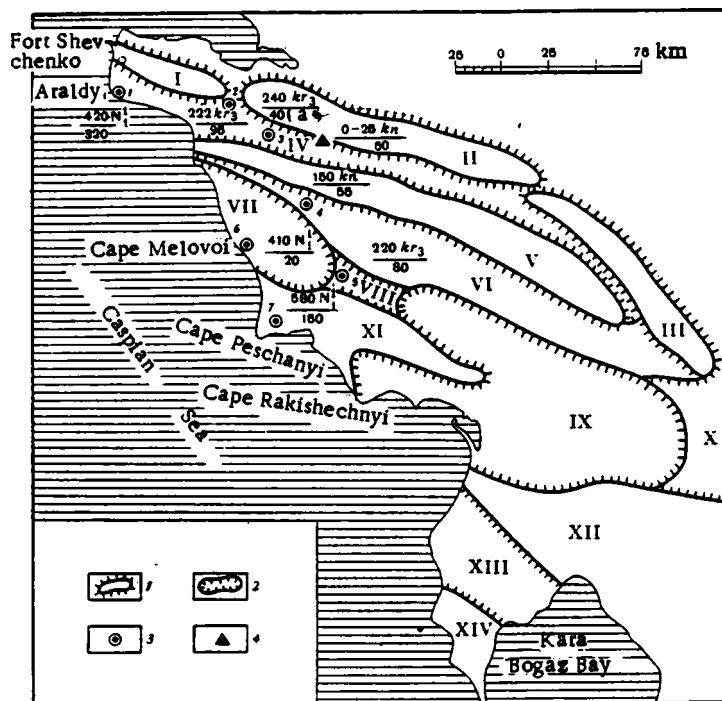


Fig. 1. Basic structural units of the South Mangyshlak Plateau, adjacent areas of the Mangyshlak Peninsula, and the northern Kara Bogaz coastal region [14]. 1) Anticlinal zones; 2) syncline zones; 3) locations with known thickness of the Maikop Series: Numerator: thickness of the Series above the ore unit (starting with the Kendzhalinsk Series, with index number of Formation that tops the section); in denominator: thickness of sub-ore and ore part of Series in the Uzunbassk and Kuyulussk Formations (a-buried portion of section); 4) Mangyshlak Mn-deposit; I) Tyubkaragansk anticline zone; II) Karatau meganticline; III) Tumgachinsk anticlinal fold line; IV) Chakyrkans syncline belt; V) Bekebashkuduk anticlinal zone; VI) Zhetybaisk structural terrace; VII) Segedyk syncline; VIII) Karaginsk saddle; IX) Karabakhinsk syncline; X) Karynzhyarsk saddle; XI) Cape Peschanyi Uplift; XII) western plunge end of the Tuakyrsk meganticline; XIII) Mazarlinsk trough; XIV) Kara Bogaz arch.

lain, across an erosional unconformity, by onlapping transgressive Middle Miocene deposits (Fig. 1, locations 2 and 3). Even further to the east, the depth of this unconformity increases. In the area of the manganese deposit, only the lower (Uzunbassk Formation) and partially the middle (Kuyulussk and Kendzhalinsk Formations) Oligocene subdivision are present. Throughout the Oligocene area, the rock are clayey, with minor silt admixture. Only in the middle portion of the Chakyrkans syncline (Lower-Middle Oligocene horizons) do sandy aleurolites occur in a small lithosome among the clays. This concentration of sandy rocks among the clays is especially interesting, as the Mn-ores are tied to the sands. A detailed description of the clayey rocks has been given [11]. For this reason, we describe them only briefly.

The clayey Oligocene deposits have been described from the Tyubkaragan Peninsula (Table 1). This section is characterized by continuous, mostly carbonate-free, aleurolitic clay beds. The limy varieties include only the lower 25 m of the section, out of the apparent 320 m total Oligocene thickness, but even there, the carbonate content is minor. The  $\text{CO}_2$  content is 1-2% and only in the basal members does it increase until the appearance of the marls (Table 1, analysis #24). Higher in the section, the clays become practically carbonate-free; their  $\text{CO}_2$  content is usually less than 1%. Smectites, with minor amount of mica layers dominate in the clay matter. Lesser amounts of illite and rare kaolinite also occur.

TABLE 1. Composition of Clayey Rocks (Drillhole #1718)

| Divisions<br>and sub-<br>divisions | Forma-<br>tion                       | Mem-<br>bers                                         | Thick-<br>ness, m                                    | Analy-<br>sis num-<br>ber | Size fraction, mm |               |                |                 | Heavy<br>fraction | CO <sub>2</sub> | C <sub>org</sub> | Mn            | Fe            | Ti            | P            | Co       | Ni        | V           | Cr         | Cu        | Pb       | Zn         | Sr          | Ba          |       |
|------------------------------------|--------------------------------------|------------------------------------------------------|------------------------------------------------------|---------------------------|-------------------|---------------|----------------|-----------------|-------------------|-----------------|------------------|---------------|---------------|---------------|--------------|----------|-----------|-------------|------------|-----------|----------|------------|-------------|-------------|-------|
|                                    |                                      |                                                      |                                                      |                           | 0.5-<br>0.25      | 0.25-<br>0.1  | 0.1-<br>0.01   | 0.01            |                   |                 |                  |               |               |               |              |          |           |             |            |           |          |            |             |             |       |
|                                    |                                      |                                                      |                                                      |                           |                   |               |                |                 |                   |                 |                  |               |               |               |              |          |           |             |            |           |          |            |             |             |       |
| Oligocene                          | Upper P <sub>3</sub>                 | Karageinsk P <sub>3</sub> <sup>3</sup> kr            | upper<br>P <sub>3</sub> <sup>3</sup> kr <sub>3</sub> | 1                         | Trace             | 0.14          | 17.52          | 82.34           | 0.15              | 0.65            | 0.20             | 0.05          | 4.32          | 0.50          | None         | 1*       | 31        | 190         | 100        | 4         | 10       | 105        | 206         | 329         |       |
|                                    |                                      |                                                      |                                                      | 2                         | Trace             | 0.04          | 15.01          | 84.95           | 0.17              | 1.00            | 0.27             | 0.07          | 4.36          | 0.51          | Trace        | 41       | 70        | 170         | 93         | 3         | 27       | 95         | 184         | 325         |       |
|                                    |                                      |                                                      |                                                      | 3                         | Trace             | Trace         | Trace          | Trace           | Trace             | 0.60            | Trace            | 0.08          | 5.41          | 0.54          | 0.1          | 30       | 48        | 220         | 120        | 25        | 35       | 100        | 165         | 316         |       |
|                                    |                                      |                                                      | middle P <sub>3</sub> <sup>3</sup> kr n <sub>2</sub> | 104                       | 4                 | Trace         | Trace          | Trace           | Trace             | Trace           | 0.58             | Trace         | 0.05          | 4.91          | 0.55         | 0.06     | 20        | 46          | 200        | 110       | 28       | 26         | 121         | 168         | 338   |
|                                    |                                      |                                                      |                                                      |                           | 5                 | 0.02          | 0.13           | 17.01           | 82.84             | 0.03            | None             | Trace         | 0.06          | 4.11          | 0.60         | 0.002    | 21        | 48          | 150        | 80        | 38       | 24         | 128         | 158         | 340   |
|                                    |                                      |                                                      |                                                      |                           | 6                 | Trace         | Trace          | Trace           | Trace             | Trace           | 0.30             | 0.12          | 0.07          | 4.10          | 0.58         | None     | 9         | 43          | 170        | 100       | 23       | 28         | 114         | 144         | 359   |
|                                    |                                      |                                                      |                                                      |                           | 7                 | Trace         | Trace          | Trace           | Trace             | Trace           | Trace            | Trace         | 0.04          | 6.55          | 0.55         | 0.1      | 21        | 48          | 180        | 100       | 20       | 16         | 115         | 147         | 411   |
|                                    |                                      |                                                      |                                                      |                           | 8                 | Trace         | Trace          | Trace           | Trace             | Trace           | Trace            | Trace         | 0.04          | 6.14          | 0.50         | 0.06     | 21        | 61          | 210        | 110       | 1        | 30         | 134         | 149         | 304   |
|                                    |                                      |                                                      |                                                      |                           | 9                 | Trace         | Trace          | Trace           | Trace             | Trace           | Trace            | Trace         | 0.05          | 5.80          | 0.55         | 0.06     | 19        | 42          | 200        | 110       | 19       | 31         | 120         | 120         | 298   |
|                                    |                                      |                                                      |                                                      |                           | 10                | 0.03          | 0.3            | 12.36           | 87.31             | 0.65            | Trace            | Trace         | 0.05          | 5.58          | 0.56         | 0.06     | 20        | 50          | 110        | 65        | 58       | 30         | 131         | 134         | 364   |
|                                    |                                      |                                                      |                                                      |                           | 11                | Trace         | 0.06           | Trace           | Trace             | Trace           | 0.35             | 0.08          | 0.08          | 4.18          | 0.54         | None     | 21        | 67          | 160        | 92        | 30       | 29         | 94          | Trace       | Trace |
|                                    |                                      |                                                      |                                                      |                           | 12                | 0.01          | 0.06           | 12.22           | 87.71             | 0.41            | 0.25             | 0.29          | 0.05          | 4.30          | 0.63         | Trace    | 28        | 55          | 150        | 85        | 14       | 35         | 116         | 128         | 350   |
|                                    | Middle P <sub>3</sub>                | lower<br>P <sub>3</sub> <sup>3</sup> kr <sub>1</sub> | 31                                                   | 13                        | Trace             | 2.18          | 23.60          | 74.22           | 0.06              | 1.50            | 0.20             | 0.16          | 4.40          | 0.78          | 0.01         | 16       | 36        | 200         | 110        | 2         | 11       | 92         | 146         | 349         |       |
|                                    |                                      |                                                      |                                                      | 14                        | Trace             | Trace         | Trace          | Trace           | Trace             | Trace           | Trace            | 0.15          | 5.84          | 0.71          | 0.1          | 25       | 57        | 160         | 100        | 14        | 20       | 98         | 138         | 352         |       |
|                                    |                                      |                                                      |                                                      | 15                        | Trace             | Trace         | Trace          | Trace           | Trace             | Trace           | Trace            | 0.09          | 4.80          | 0.61          | 0.1          | 1        | 48        | 150         | 120        | 18        | 10       | 101        | 151         | 383         |       |
|                                    |                                      | Kendz-<br>halinsk<br>P <sub>3</sub> <sup>3</sup> kr  | 55                                                   | 16                        | None              | 0.03          | 12.96          | 87.01           | Trace             | None            | 0.07             | 0.05          | 4.05          | 0.61          | None         | 42       | 58        | 200         | 110        | 68        | 32       | 120        | 142         | 287         |       |
|                                    |                                      |                                                      |                                                      | 17                        | 0.12*             | 3.72*         | 32.73*         | 63.44*          | Trace             | 0.25            | 0.16             | 0.15          | 4.11          | 0.64          | 0.001        | 24       | 53        | 210         | 120        | 35        | 26       | 98         | 149         | 320         |       |
|                                    |                                      |                                                      |                                                      | 18                        | Trace             | Trace         | Trace          | Trace           | Trace             | 0.20            | 0.14             | 0.05          | 3.59          | 0.64          | None         | 34       | 46        | 190         | 110        | 25        | 26       | 129        | 149         | 316         |       |
|                                    |                                      | Kuyulusk<br>P <sub>3</sub> <sup>3</sup> kr           | 30                                                   | 19                        | Trace             | Trace         | Trace          | Trace           | Trace             | 5.40*           | 0.14             | 0.48*         | 4.51          | 0.59          | Trace        | 73       | 59        | 200         | 100        | 12        | 20       | 98         | 136         | 254         |       |
|                                    |                                      |                                                      |                                                      | 20                        | Trace             | 0.05          | 24.58          | 75.37           | 0.15              | 0.10            | 0.20             | 0.05          | 4.02          | 0.56          | 0.06         | 8        | 39        | 170         | 100        | 25        | 24       | 117        | 151         | 299         |       |
|                                    |                                      |                                                      |                                                      | 21                        | Trace             | 0.01*         | 0.08*          | 99.91*          | 0.084             | 7.04*           | Her              | 0.52*         | 8.41          | 0.48          | 0.005        | 50       | 67        | 140         | 100        | 20        | 6        | 77         | 163         | 252         |       |
|                                    | Lower<br>P <sub>3</sub> <sup>1</sup> | Uzunbask<br>P <sub>3</sub> <sup>1</sup> uz           | 65                                                   | 22                        | Trace             | 0.01          | 17.47          | 82.52           | 0.06              | 0.25            | 0.27             | 0.08          | 3.72          | 0.56          | None         | 13       | 13        | 180         | 75         | 10        | 35       | 108        | 160         | 299         |       |
|                                    |                                      |                                                      |                                                      | 23                        | Trace             | 1.38          | 24.59          | 74.02           | 0.33              | 1.65            | 1.74*            | 0.05          | 3.82          | 0.56          | Trace        | 29       | 29        | 210         | 100        | 106*      | 24       | 134        | 219         | 316         |       |
|                                    |                                      |                                                      |                                                      | 24                        | Trace             | Trace         | Trace          | Trace           | Trace             | 16.20*          | 0.50             | 0.16          | 3.32          | 0.33          | 0.006        | 21       | 21        | 110         | 88         | 55        | 5        | 93         | 477*        | 252         |       |
| Range of measured composition      |                                      |                                                      |                                                      |                           | None-<br>0.12     | 0.04-<br>3.72 | 0.08-<br>32.73 | 63.44-<br>99.91 | Trace -<br>0.65   | None-<br>16.20  | None-<br>1.74    | 0.04-<br>0.52 | 3.32-<br>8.41 | 0.33-<br>0.78 | None-<br>0.1 | 1-<br>73 | 13-<br>70 | 110-<br>210 | 75-<br>120 | 1-<br>106 | 5-<br>35 | 77-<br>134 | 120-<br>477 | 252-<br>411 |       |
| Average composition                |                                      |                                                      |                                                      |                           | 0.01              | 0.36          | 17.73          | 81.83           | 0.17              | 0.5             | 0.18             | 0.07          | 4.60          | 0.57          | 0.03         | 26       | 47        | 180         | 100        | 23        | 23       | 110        | 148         | 309         |       |

\*Values not established through calculation of average values, here and in the following tables.

Note. In the present and the following tables the heavy fraction is given in percentages from the 0.1-0.01 mm fraction; CO<sub>2</sub>, organic C, Mn, Fe, Ti, P, in %, established by chemical analysis; Co, V, and Cr by semiquantitative spectral analysis; other elements by x-ray fluorescence analysis, 10<sup>-4</sup>.

TABLE 2. Average Element Composition of Clayey Deposits

| Drillhole number                                                   | Mn    | Fe   | Ti   | P     | Co | Ni | V   | Cr  | Cu | Pb | Zn  | Sr  | Ba  |
|--------------------------------------------------------------------|-------|------|------|-------|----|----|-----|-----|----|----|-----|-----|-----|
| 1718                                                               | 0,07  | 4,60 | 0,57 | 0,03  | 26 | 47 | 179 | 100 | 23 | 23 | 110 | 148 | 309 |
| 9113                                                               | 0,06  | 4,34 | 0,47 | 0,12  | 39 | —  | 200 | 150 | 96 | 33 | 116 | 226 | 322 |
| 1805                                                               | 0,06  | 3,24 | 0,40 | 0,06  | 19 | 35 | 110 | 57  | 34 | 39 | 107 | 288 | 292 |
| av. values in clays                                                | 0,06  | 4,06 | 0,48 | 0,07  | 28 | 41 | 163 | 102 | 51 | 32 | 110 | 241 | 308 |
| Clarke values of sedimentary rocks, according to A. P. Vinogradova | 0,067 | 3,33 | 0,45 | 0,077 | 20 | 95 | 130 | 100 | 57 | 20 | 80  | 450 | 800 |

Note. Mn, Fe, Ti and P concentration values in percentages; other elements: in 10<sup>-4</sup>%.

Between 12-25% detrital matter occurs in the clayey rocks; this value changes from layer-to-layer. On the whole, it remains at generally the same level in the section. The detrital grains are generally of silt size. Individual sand grains also occur. These grains are composed of quartz, rarely plagioclase feldspar. Occasionally, certain layers are enriched in glauconite, less frequently, in zeolites. Gel-like organic matter is typical, with a tendency to form clots. In addition, pyritized fish fossils also occur, and plant tissue fragments. Finely disseminated pyrite and melnikovite occurs generally in the clays; occasionally siderite (Table 1, analysis No. 21). A generally relatively increased Fe content in the clays is related to suflide mineralization.\*

In analyzing the Oligocene portion of the section (drillhole No. 1718) in terms of several chemical elements (Table 1), it turned out that most of them had values close to clarke concentrations. With rare exceptions, these values remained constant throughout the whole section. The Fe values were somewhat higher, the Sr and Ba values lower than the clarke values. Mn was at the clarke level and only on two occasions (Table 1; analyses No. 19 and No. 20) did its concentration reach about 0.5%.

The Oligocene clayey deposits occurred not only in the Tyubkaragan area. They stretch from drillhole No. 1718 for several tens of kilometers toward the SE, into the vicinity of the ore deposit, without almost any change in their lithological and geochemical characteristics. For comparison, Table 2 shows the mean element concentrations in the clayey rocks of the described section and two drillholes, located in the immediate vicinity where the sandy productive unit of the ore deposit peters out.

In the transitional zone between the clayey and sandy deposits the silt content in the clay starts to increase and there is a tendency for size increase in the detrital grains. Typically, increase in the amount and size of clastic matter occurs only in a given stratigraphic interval that roughly corresponds to the boundary between the Lower and Middle Oligocene. This "embryonic" sandy unit is under- and overlain by clays with usually low silt content. Approaching the ore deposit, within this unit the manganese content gradually increases. Thus, 5-7 km from the main ore deposit, the sandy deposits start to display small (maximum 1 cm) carbonate concretions with a maximum 25% Mn content. The rocks that enclose the concretions contain less Mn than the clarke value.

The productive ore body is composed of sandy-silty deposits. The area covered by these rocks is about 50 km<sup>2</sup>, their thickness is maximum 30 m. The rocks occur in a zone where the northern limb of the Chakyrkansky syncline meets the Karatau meganticline. The sandy unit occupies an interval in the section that corresponds to the lower part of the Middle Oligocene (Kuyulussk Formation) that conformably overlies the Lower Oligocene clayey rocks. In the southern part of the region where sandy deposits are present, they are conformably overlain by Middle Oligocene clays of higher horizons. To the north, near Karatau, Middle, and further on, Upper Miocene beds overlie the productive ore body across an erosional unconformity. The transition from clayey rocks of the units, beneath and above the ore

\*The organic C and Fe content in the clay layers is generally somewhat higher than shown in Table 1. This results from the fact that the analyzed samples lacked significant organic concentrations. Such matter, in turn, is associated with Fe-sulfides.

TABLE 3. Element Composition in Terrigenous Rocks of the Ore Unit

| Number of analysis                                                             | CO <sub>2</sub> | C <sub>org</sub> | Mn        | Fe        | Ti        | P         | Co    | Ni    | V      | Cr     | Cu      | Pb   | Zn    | Sr      | Ba      |
|--------------------------------------------------------------------------------|-----------------|------------------|-----------|-----------|-----------|-----------|-------|-------|--------|--------|---------|------|-------|---------|---------|
| Rocks between ore beds                                                         |                 |                  |           |           |           |           |       |       |        |        |         |      |       |         |         |
| 1                                                                              | 12,75           | None             | 0,08      | 1,90      | 0,32      | None      | 8     | 46    | 92     | 72     | 30      | 7    | 50    | 130     | 364     |
| 2                                                                              | 0,15            | "                | 0,08      | 2,04      | 0,35      | "         | 10    | 72    | 140    | 75     | 17      | 9    | 75    | 365     | 549     |
| 3                                                                              | None            | "                | 0,03      | 2,20      | 0,30      | "         | 12    | 58    | 130    | 60     | 32      | 12   | 56    | 347     | 570     |
| 4                                                                              | "               | "                | 0,02      | 0,23*     | 0,26      | 0,04      | 20    | 43    | 100    | 91     | 21      | 13   | 66    | 364     | 616     |
| 5                                                                              | 2,10            | "                | 0,04      | 2,23      | 0,31      | 0,06      | 20    | 48    | 135    | 200*   | 18      | 7    | 73    | 321     | 551     |
| 6                                                                              | None            | "                | 0,04      | 1,95      | 0,31      | 0,06      | 18    | 39    | 80     | 50     | None    | 16   | 63    | 285     | 610     |
| 7                                                                              | "               | "                | 0,04      | 2,23      | 0,31      | 0,05      | —     | —     | —      | —      | —       | —    | —     | —       | —       |
| Composition range                                                              | None — 12,75    | "                | 0,02—0,08 | 0,23—2,23 | 0,26—0,35 | None—0,06 | 8—20  | 39—72 | 92—140 | 50—200 | None—32 | 7—16 | 50—75 | 130—365 | 364—616 |
| Av.                                                                            | —               | "                | 0,04      | 2,09      | 0,29      | 0,03      | 15    | 51    | 113    | 70     | 20      | 11   | 64    | 336     | 579     |
| Rocks that contain concretions and karlofites directly                         |                 |                  |           |           |           |           |       |       |        |        |         |      |       |         |         |
| 8                                                                              | 0,15            | "                | 0,07      | 1,56      | 0,29      | Her       | 21    | 76    | 116    | 62     | None    | 9    | 44    | 393     | 515     |
| 9                                                                              | None            | "                | 0,07      | 1,95      | 0,26      | 0,05      | 20    | 43    | 200*   | 20     | 18      | 15   | 65    | 475     | 603     |
| 10                                                                             | "               | "                | 0,08      | 1,78      | 0,31      | 0,04      | 22    | 55    | 60     | 60     | 30      | 14   | 71    | 300     | 585     |
| 11                                                                             | "               | 0,16*            | 0,05      | 2,13      | 0,30      | 0,05      | 20    | 36    | 60     | 200*   | None    | 6    | 64    | 433     | 576     |
| 12                                                                             | "               | None             | 0,05      | 1,96      | 0,33      | 0,06      | 23    | 53    | 100    | 100    | 20      | 12   | 66    | 387     | 587     |
| 13                                                                             | "               | "                | 0,06      | 1,95      | 0,31      | 0,07      | 20    | 33    | 120    | 150    | 50      | 9    | 70    | 220     | 577     |
| 14                                                                             | 6,25            | "                | 0,03      | 2,23      | 0,26      | 0,12*     | 25    | 29    | 70     | 60     | 16      | 8    | 56    | 284     | 504     |
| 15                                                                             | None            | "                | 0,03      | 1,95      | 0,26      | 0,06      | —     | —     | —      | —      | —       | —    | —     | —       | —       |
| Composition range                                                              | None —          | "                | 0,03—0,08 | 0,79—2,50 | 0,26—0,33 | None—0,12 | 20—25 | 29—76 | 60—200 | 20—200 | None—50 | 8—15 | 44—71 | 220—475 | 504—603 |
| Av. composition                                                                | —               | "                | 0,05      | 1,95      | 0,29      | 0,05      | 21    | 46    | 87     | 75     | 19      | 10   | 62    | 356     | 564     |
| Average element content in terrigenous rocks of productive ore beds in general |                 |                  |           |           |           |           |       |       |        |        |         |      |       |         |         |
| Av. composition                                                                | —               | "                | 0,04      | 2,02      | 0,29      | 0,04      | 18    | 48    | 100    | 72     | 20      | 10   | 63    | 346     | 571     |

Note. The CO<sub>2</sub>, organic C, Mn, Fe, Ti, and P content established by chemical analysis, in percentages; Co, V, Cr — approximate quantitative spectral analysis values ("spill" method, 10<sup>-4</sup>%; other elements: established by x-ray fluorescence, 10<sup>-4</sup>%).



TABLE 4. Composition of Carbonate Concretions, Based on Carbonate Analysis, in %

| Sample No. | MHO   | R <sub>2</sub> O <sub>3</sub> | CaO   | MnO   | MgO  | P <sub>2</sub> O <sub>5</sub> | CO <sub>2</sub> | C    | Total |
|------------|-------|-------------------------------|-------|-------|------|-------------------------------|-----------------|------|-------|
| 159        | 49,34 | 2,47                          | 17,48 | 8,82  | 1,07 | 0,09                          | 19,50           | None | 98,68 |
| 162        | 36,90 | 4,30                          | 7,76  | 20,78 | 3,35 | 0,02                          | 21,55           | 0,22 | 94,86 |
| 175        | 61,94 | 2,41                          | 2,22  | 17,16 | 1,04 | 0,01                          | 11,80           | None | 97,01 |
| 166-v      | 61,35 | 1,97                          | 17,05 | 2,14  | 0,83 | 0,32                          | 12,55           | 0,12 | 96,32 |

body, to the ore-bearing sandy deposits between them is fast. The result is the sharply defined outline of the productive rock body. Clayey deposits that directly enclose the productive rock body in terms of composition and geochemical characteristics are close to those clays that occur beyond this area. The Mn content in clays beneath the ore body is 0.05%; there is a definite trend in the Mn distribution in clays; with decreasing distances from the ore deposit the Mn content decreases in the clay. In drillhole No. 1718 the content was 0.07%, closer to the ore body 0.06%, and just above the deposit itself: 0.05%.

The terrigenous rocks of the producing unit are composed basically of sandy aleurolites and fine-grained sandstones. Quartz predominates in the detrital grain fraction, minor amounts of altered feldspar grains (mostly acidic plagioclase) also occur. In certain layers significant amounts of glauconite, minerals of the epidote group, and hydrated biotite occurs. Minor amounts of altered terrigenous rocks fragments, zircon, tourmaline, rutile, apatite, sphene, anatase-brookite group minerals, ilmenite and leucoxene grains occur in minor quantities. Authigenic varieties were typical: opal, less frequently zeolites. Part of the glauconite may be of authirgenic derivation. The rocks often contained sponge spicules, molluscan fragments, arthropoda, and microfossils. The interstices between detrital fragments was filled by clayey matter of smectitic, less frequently illitic composition. In addition to these basic components, chlorite, quartz and heulandite-group zeolites occur in very minor amounts but persistently. Opal occurs in the cement of layers that are enriched in sponge spicules. Cementation is not strong; the effective rock porosity, according to Dombrovskaya [10], is 39-49%, the specific gravity: 1.44-1.62 g/cm<sup>3</sup>.

Generally, the described rocks are carbonate-free and contain no organic matter (Table 3). Only in instances when the producing ore unit is directly overlain by Miocene lime-stones do the highest horizons in the ore sequence contain secondary carbonate cement (Table 3, analysis No.1). Occasionally, minor increase in the carbonate content of the rock is caused by the presence of calcite-bearing shells. In the sandy rocks calcite concretions occur rarely.

Texturally, the described rocks are either homogenous, or display crude, slightly visible, faint horizontal layering. Only in two exposures was cross-stratification observed, with typical festoon cross-bedding of curved layers. Typically, the composition, structure and texture of the discussed sediments in all sections of the producing ore unit were approximately identical. It is especially interesting that none of the significant exceptions to this involved rocks that directly enclosed Mn-ores, or such "barren" beds that separate ore-bearing horizons. These deposits have not only similar petrographic and granulometric makeup, but are also similar in their geochemical features. Table 3 shows that the composition of all the studied chemical elements in the productive lithosome have generally uniform composition that is somewhat lower than the clarke values. In contrast with clays, the sandy rocks have lower Mn, Fe, Ti, Co, V, Cr, Cu, Pb, and Zn composition and slightly higher Sr and Ba content.

The manganese ores occur in the upper part of the producing unit and are concentrated in a 10-15 m thick interval of the section where they occur in a few beds and lenses. There they are separated by sandy rock layers that carry no marks of mineralization. The number and thickness of the ore-bearing beds varies: in the NW part of the deposit three or four productive beds occur, the thickest of them is 2.5-3 m.

The ore beds are composed of a number of layers that are enriched in Mn-concretions, embedded in a sandy-aleurolitic mass. In addition to concretions, these beds sometimes contain secondary, earthy-sooty Mn-hydroxides. These occur either relatively evenly dispersed in the sandy bed, or in the form of dense concretions. These features usually are

TABLE 5. Composition of Carbonate Concretions, Based on Silicate Analysis, in %

| Component                      | Sample number |       |       |       | Component                     | Component number |       |       |       |
|--------------------------------|---------------|-------|-------|-------|-------------------------------|------------------|-------|-------|-------|
|                                | 166-a         | 41-a  | 160   | 44    |                               | 166-a            | 41-a  | 160   | 44    |
| SiO <sub>2</sub>               | 50,52         | 39,10 | 30,46 | 24,57 | K <sub>2</sub> O              | 2,24             | 2,08  | 1,36  | 1,27  |
| TiO <sub>2</sub>               | 0,33          | 0,31  | 0,20  | 0,26  | H <sub>2</sub> O <sup>+</sup> | 2,25             | 2,34  | 2,20  | 2,46  |
| Al <sub>2</sub> O <sub>3</sub> | 7,20          | 3,55  | 4,82  | 3,73  | H <sub>2</sub> O <sup>-</sup> | 1,14             | 1,48  | 1,46  | 1,01  |
| Fe <sub>2</sub> O <sub>3</sub> | 1,84          | 6,96  | 2,64  | 5,38  | CO <sub>2</sub>               | 11,00            | 16,45 | 20,20 | 21,50 |
| FeO                            | —             | —     | —     | —     | C                             | None             | 0,10  | 0,82  | None  |
| MnO                            | 0,30          | 13,69 | 20,63 | 23,52 | P <sub>2</sub> O <sub>5</sub> | —                | 0,21  | 0,05  | 1,55  |
| MnO <sub>2</sub>               | 3,91          | None  | 1,52  | Her   | BaO                           | 0,09             | 0,04  | 0,02  | —     |
| CaO                            | 16,88         | 10,78 | 9,90  | 8,99  | SrO                           | 0,09             | 0,03  | 0,05  | —     |
| MgO                            | 0,52          | 0,83  | 1,56  | 0,84  | SO <sub>3</sub>               | None             | —     | None  | None  |
| Na <sub>2</sub> O              | 2,16          | 1,71  | 1,58  | 1,49  | None                          | 100,47           | 99,66 | 99,48 | 99,43 |

TABLE 6. Recalculation to Carbonate Composition

| Component                                       | Sample number |       |       |       |       |       |       |       |
|-------------------------------------------------|---------------|-------|-------|-------|-------|-------|-------|-------|
|                                                 | 159           | 162   | 175   | 166-V | 166-a | 41-a  | 160   | 44    |
| Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> | —             | —     | —     | 0,69  | None  | 0,46  | 0,11  | 2,18  |
| CaCO <sub>3</sub>                               | 31,20         | 13,85 | 3,96  | 30,34 | 24,97 | 18,95 | 7,90  | 12,80 |
| MnCO <sub>3</sub>                               | 14,31         | 33,71 | 26,25 | —     | None  | 22,20 | 12,80 | 38,10 |
| MgCO <sub>3</sub>                               | 0,36          | 4,82  | —     | —     | —     | —     | —     | —     |

Note. Recalculation to Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> took place only when P<sub>2</sub>O<sub>5</sub> > 0.1%. In samples 159 and 162 the MgO excess was 0.9% and 1.03%, respectively. In sample 175 the MnO excess was 0.97%, MgO: 1.04%; in sample 166-v, the excess of CaO was 0.69%, MnO: 2.14%, MgO: 0.83%; in sample 166-a, the excess was 3.02%.

found in the top portion of the upper ore bed, when the bed occurs close to the surface. The concentration of concretions in the ore beds varies: in the richest beds this value reaches 75% of the total rock volume, but as the producing unit peters out, the concretions gradually disappear and only a few individual concretions occur. A great variety of concretion shapes exist, from the relatively simple, rounded or oblate forms, to complex branching types. Concretion sizes vary from fractions of one cm to tens of cm, reaching 1 m. All concretions contain sandy-aleurolitic matter, cemented by ore matter, occasionally with calcite admixture. Carbonate, oxide-carbonate and oxide concretions exist in terms of chemical composition.\* Strictly speaking, only the carbonate type may be defined as concretions among the discussed concretionary features. Their oxidized varieties that contain a flattened nucleus and a thick surrounding shell are secondary. They form through oxidation and accompanying growth of the original carbonate concretions, as discussed in greater detail in the following. Certain authors called these features geodes [8]. This is incorrect: geodes form around cavities, filled by mineral matter from the periphery toward the center. However, in our case the cavity forms through transformation of the original, dense concretion. These genetically defined features we propose to name kariolites, from the Greek word *καριον* = opex(nut).

The carbonate concretions usually are rounded or bun-shaped. Their exteriors recall gray, sandy limestones with typical vesicular surfaces. Cavities occur in the carbonate body of the concretions, partially filled with iron ochre, formed after pyrite. The main minerals of the carbonate components in the concretions include rhodochrosite, Mn-calcite, and calcite that cement the sandy matter. The relationship between the detrital substrate, the carbonate cement, and the Mn- and Ca-carbonates in this cement is variable. Tables 4-6 indicate that the carbonate concentration varies between 20-50% in the rocks. In most concentrations the MnCO<sub>3</sub> content predominates maximum sixfold over the CaCO<sub>3</sub> content. Reverse

\*The carbonate concretions also include ores with 5% Mn-oxide content, and the oxide concretions contain carbonates with less than 5% Mn. Mixed ore types contain oxides and carbonates in variable ratios.

TABLE 7. Element Content in Carbonate Concretions

| Sample number       | Mn         | Fe        | Ti        | P          | C      | Co   | Ni    | V      | Cu    | Pb    | Zn     | Sr      | Ba      |
|---------------------|------------|-----------|-----------|------------|--------|------|-------|--------|-------|-------|--------|---------|---------|
| 159                 | 6,84       | 1,80      | 0,19      | 0,04       | None   | 8    | 15    | 80     | 20    | 112   | 183    | 799     | 726     |
| 162                 | 16,11      | 3,60      | 0,16      | 0,01       | 0,22   | 20   | 20    | 50     | 30    | 115   | 162    | 325     | 209     |
| 175                 | 13,31      | 2,70      | 0,22      | 0,005      | None   | 20   | 30    | 100    | 30    | 117   | 182    | 241     | 268     |
| 166-v               | 1,66       | 1,90      | 0,22      | 0,14       | 0,12   | 10   | 50    | 80     | 15    | 11    | 48     | 361     | 386     |
| 166-a               | 2,68       | 1,29      | 0,20      | None       | None   | 70   | 50    | 80     | 20    | 10    | 61     | 756     | 756     |
| 41-a                | 10,54      | 4,87      | 0,19      | 0,09       | 0,10   | 20   | 40    | 150    | 30    | 5     | 29     | 252     | 356     |
| 160                 | 16,85      | 1,85      | 0,12      | 0,02       | 0,82   | 20   | 20    | 100    | 30    | 11    | .85    | 420     | 178     |
| 40                  | 18,11      | 3,76      | 0,15      | 0,68*      | None   | 30   | 10    | 20     | 30    | —     | —      | —       | —       |
| Composition range   | 1,66—18,11 | 1,29—4,87 | 0,12—0,22 | 0,005—0,68 | 0—0,82 | 8—70 | 10—50 | 20—150 | 15—30 | 5—117 | 29—185 | 252—799 | 178—756 |
| Average composition | —          | 2,64      | 0,18      | 0,04       | 0,16   | 24   | 29    | 82     | 25    | 68    | 121    | 450     | 411     |

Note. The Mn, Fe, Ti, P, and C compositions given in percentages, the rest of the elements: in  $10^{-4}\%$ .

TABLE 8. Composition of the Sandy Kariolite Nucleus

| Sample number       | CO <sub>2</sub> | C    | Mn        | Fe        | Ti        | P         | Co   | Ni     | V      | Cr     | Cu   | Pb   | Zn    | Sr       | Ba      |
|---------------------|-----------------|------|-----------|-----------|-----------|-----------|------|--------|--------|--------|------|------|-------|----------|---------|
| 1                   | 0,55            | —    | 0,08      | 3,63      | 0,34      | None      | 32   | 100    | 150    | 80     | 32   | 22   | 30    | 218      | 506     |
| 2                   | 0,15            | None | 0,08      | 1,58      | 0,29      | 0,11      | 4    | 15     | 77     | 46     | 22   | 7    | 30    | 923      | 508     |
| 3                   | None            | »    | 0,07      | 2,79      | 0,31      | 0,04      | 20   | 40     | 100    | 100    | 30   | 20   | 70    | 400      | 400     |
| 4                   | »               | »    | 0,10      | 2,43      | 0,33      | 0,02      | 10   | 30     | 200    | 100    | 20   | 25   | 80    | 200      | 400     |
| 5                   | »               | »    | 0,10      | 5,82*     | 0,31      | 0,03      | 8    | 30     | 100    | 100    | 20   | 30   | 75    | 300      | 400     |
| 6                   | »               | »    | 0,09      | 2,11      | 0,30      | 0,10      | 15   | 49     | 100    | 100    | 23   | 13   | 58    | 197      | 612     |
| 7                   | 0,55            | »    | 0,10      | 1,73      | 0,25      | 1,62      | 7    | 20     | 100    | 100    | 15   | 15   | —     | 1500*    | 600     |
| 8                   | —               | —    | 0,10      | 2,30      | 0,50      | 2,10      | —    | 12     | 80     | 80     | 7    | 8    | 41    | 648      | 509     |
| 9                   | —               | —    | 0,20      | 2,70      | 0,30      | 0,05      | 15   | 30     | 100    | 100    | 40   | 15   | —     | 1500*    | 600     |
| 10                  | —               | —    | 0,04      | 1,90      | 0,50      | 0,10      | 7    | 20     | 90     | 100    | 20   | 10   | 70    | 300      | 500     |
| 11                  | —               | —    | 0,06      | 2,50      | 0,30      | 0,08      | 7    | 20     | 100    | 100    | 30   | 20   | 50    | 200      | 400     |
| Composition range   | None—0,55       | None | 0,04—0,20 | 1,58—5,82 | 0,25—0,50 | None—2,10 | 4—32 | 12—100 | 77—200 | 46—100 | 7—40 | 7—30 | 30—80 | 218—1500 | 400—600 |
| Average composition | —               | »    | 0,09      | 2,37      | 0,33      | 0,05      | 13   | 33     | 109    | 91     | 23   | 17   | 56    | 376      | 494     |

Note. The CO<sub>2</sub>, organic C, Mn, Fe, Ti, and P content was determined by chemical analysis; the rest of the elements by x-ray fluorescence and spectral analysis (approximate-quantitative-"spill"-method), in  $10^{-4}\%$ .

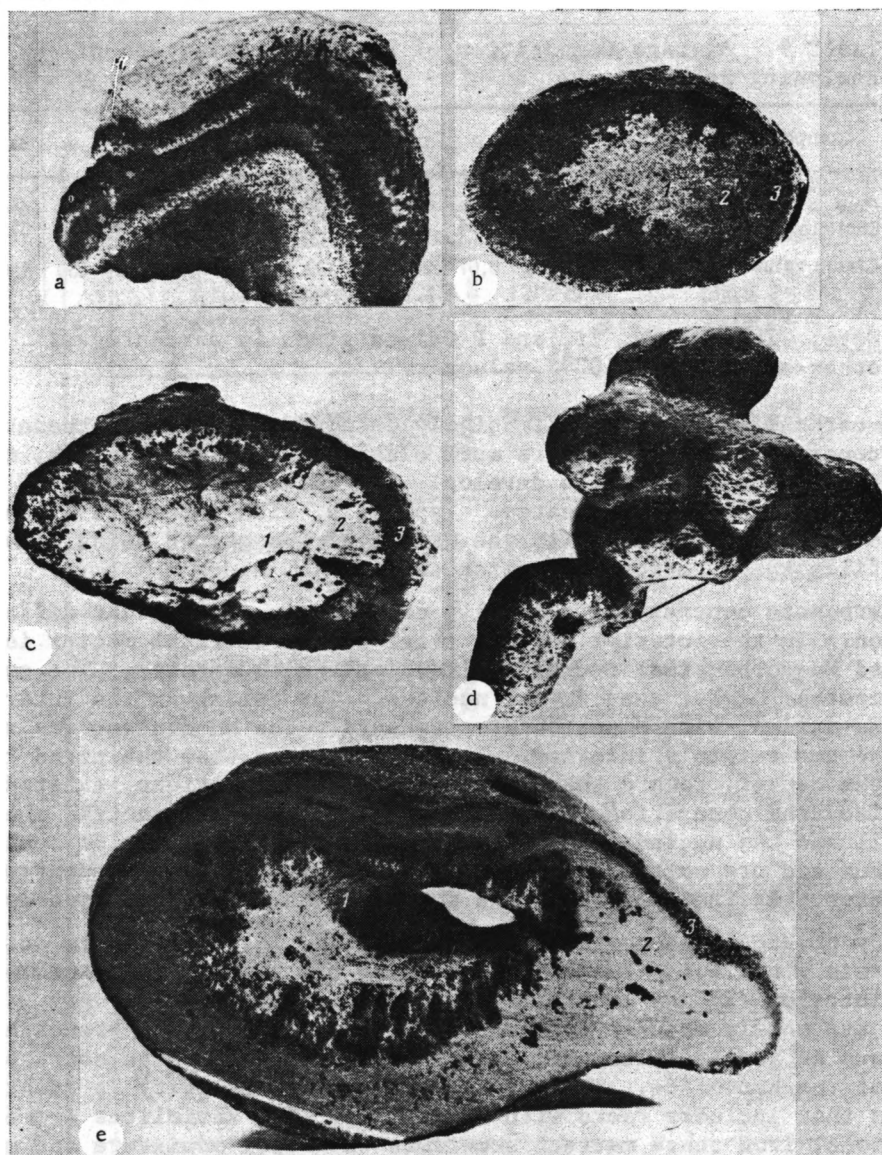


Fig. 2. Types of manganese- and manganese ore concretions and kariolites. a) Calcitic, slightly manganitic concretion of concentric structure: dark bands have relatively high Mn content; b, c) oxide-carbonate concretion (actual size): 1) core (sandy matter, cemented by Mn-carbonates); 2) band, with partly oxidized Mn-carbonates; 3) band, with Mn-oxides and relicts of Mn-carbonates; d) oxidized kariolite (actual size) 1) sandy core; 2) interior ore band; 3) exterior ore band; e) oxidized, branching kariolite.

ratios are rare. In samples in which  $\text{MnCO}_3$  predominates over  $\text{CaCO}_3$ , the Mn content ranges between 10-18%; being 15%, on the average. The average composition of elements in the carbonate ores is shown in Table 7.

The concretions are either of concentric or of homogeneous, non-zoned structure. The concentric shells differ in terms of the carbonate composition and are especially well defined when they contain oxidized Mn-carbonates. Such low-Mn-calcite concretions with oxidized Mn-carbonates are shown in Fig. 2a. The  $\text{CaCO}_3$  concentration in the lighter shells of the concretion is about 30%; Mn: 1.66%; in the darker shells:  $\text{CaCO}_3$ : 25%, Mn: 2.68%. In the nonzoned, partially oxidized concretions the Mn-oxides have evenly pigmented the carbonate mass or formed veinlike and mottled concentrations.

TABLE 9. Average Composition of Kariolite Cores and of Enclosing Rocks

| Component       | Mn   | Fe   | Ti   | P    | Co | Ni | V   | Cr  | Cu | Pb | Zn | Sr  | Ba  |
|-----------------|------|------|------|------|----|----|-----|-----|----|----|----|-----|-----|
| Core            | 0,09 | 2,37 | 0,33 | 0,05 | 13 | 33 | 109 | 90  | 23 | 17 | 56 | 376 | 494 |
| Enclosing rocks | 0,04 | 2,02 | 0,29 | 0,04 | 18 | 48 | 100 | 72  | 20 | 10 | 63 | 346 | 571 |
| Clarke values   | 0,07 | 3,33 | 0,45 | 0,07 | 20 | 95 | 130 | 100 | 57 | 20 | 80 | 450 | 800 |

Note. The Mn, Fe, Ti, and P values given in percentages; other elements in  $10^{-4}\%$  values.

When the Mn-carbonates are more intensively oxidized and mixed carbonate-oxide ores form, the zonal concretion structures are more clearly expressed (Fig. 2b, c). A clearly defined nucleus and surrounding shells develop. The nucleus is composed of sandy matter; loose, or cemented by Mn and Ca-carbonates. Typically, with increased oxidation of the Mn-carbonates the porosity increases (to the extent of the matter being friable) in the sandy mass that fills the interior concretion cavity.

The oxide-carbonate concretions generally contain two shells that differ in the ore matter composition. In the interior shell 2 (Fig. 2a, b) detrital matter is cemented by partially oxidized Mn-carbonates; occasionally jointly with calcite. The cementation was firm and the Mn-content higher than in the nucleus. The cement in the interior shell No. 3 was composed of Mn-oxides, with Mn-carbonate remnants. The Mn-content was significantly higher than in the concretion's interior. It is emphasized that the trend toward increased Mn-content from the center, toward the periphery of the concretions, existed in all concretions. In the discussed concretions the boundary between the concentric shells and between the interior shell and the nucleus is not very sharp. The sharpness of boundary increases between the nucleus and ore portion of the concretion with increasing degree of oxidation of the Mn-carbonates. At the same time, the shape of the concretion becomes more complex.

Concretionary products, composed of Mn-oxides (Fig. 2d, e) are here defined as kariolites. They contain a nucleus (1) and a surrounding ore shell. This shell is further subdivided into an interior (2) and exterior (3) subshell. Their forms vary from ellipsoidal, with ridges that are poorly or well defined (Fig. 2d), to complexly branching (Fig. 2e) types. The nucleus is partly filled with sandy matter and its shape corresponds to the general outline of the kariolite. The matter that fills the cavity is identical in composition to the bed that includes rocks with kariolites. The kariolites are either "friable" or cemented by loose, iron ochre matter, sometimes with opal admixture and minor amounts of Mn-oxides. The effective porosity of the "friable" sandy nucleus matter is 50%, the density  $1.45 \text{ g/cm}^3$  and its Mn content does not exceed a few tenths of one percent (0.09%, on the average; Table 8). The carbonate content is only sporadic but if it does occur, the  $\text{CO}_2$ -content is a fraction of one percent, and organic matter is totally absent. The Fe, Ti, P and trace element concentrations remain at Clarke or even lower levels. Typically, the values of these elements in kariolite nuclei are very close to concentration values found in the enclosing rocks (Table 9).

The shell of the kariolites usually consists of two subshells; an interior and an exterior shell (Fig. 2e). The interior subshell No. 2 forms the bulk of the shell and consists of dense (12-15% porosity), bluish-black ore mass with polycrystalline luster. Thickness varies between a few millimeters and 1.5-2 cm. The contact with the nucleus is sharp, the interior surface that faces the internal kariolite cavity is smooth or hummocky with nodular growth features. The exterior subshell represents a peculiar kariolite "lining," located between the enclosing rock and the dense ore matter. This subshell most often is a film or thin (few mm thick), brownish-black layer, composed of friable (40-45% porosity), earthy Mn-oxides; sometimes with minor iron oxide admixture. Occasionally, the concretions contain individual iron shells. The shells usually are of the interior subshell variety, with thickness of maximum 5 mm.

Both subshells contain sandy matter, cemented by Mn-oxides that usually form cryptocrystalline aggregates. The ore matter does not only fill interstices between detrital grains and cover them with a continuous film but also intrudes into the grains through hair frac-

TABLE 10. Composition of Oxidized Manganese Ores, in %

| Com-<br>ponents                     | No. of analyses |       |       |        |       |        |        |        |        |       |       |       |
|-------------------------------------|-----------------|-------|-------|--------|-------|--------|--------|--------|--------|-------|-------|-------|
|                                     | 1               | 2     | 3     | 4      | 5     | 6      | 7      | 8      | 9      | 10    | 11    | 12    |
| SiO <sub>2</sub>                    | 37,95           | 36,80 | 25,93 | 36,61  | 41,93 | 39,34  | 44,24  | 48,24  | 37,16  | 47,48 | 34,24 | 43,66 |
| TiO <sub>2</sub>                    | 0,19            | 0,27  | 0,22  | 0,23   | 0,31  | 0,23   | 0,32   | 0,32   | 0,15   | 0,24  | 0,23  | 0,27  |
| Al <sub>2</sub> O <sub>3</sub>      | 9,16            | 4,19  | 3,94  | 11,80  | 5,75  | 11,90  | 6,55   | 6,90   | 5,46   | 6,10  | 5,72  | 6,38  |
| Fe <sub>2</sub> O <sub>3</sub>      | 3,57            | 4,89  | 5,47  | 3,26   | 4,59  | 3,45   | 4,26   | 3,79   | 2,83   | 1,90  | 3,28  | 2,34  |
| FeO                                 | —               | —     | —     | —      | —     | —      | —      | —      | —      | —     | —     | —     |
| MnO                                 | 1,44            | 3,12  | 3,07  | 1,13   | 1,87  | 0,99   | 1,38   | 1,87   | 2,20   | 2,25  | 2,44  | 2,46  |
| MnO <sub>2</sub>                    | 35,82           | 26,52 | 43,98 | 36,05  | 32,82 | 25,01  | 30,52  | 25,21  | 37,84  | 33,99 | 37,67 | 20,08 |
| CaO                                 | 2,70            | 7,97  | 3,03  | 2,05   | 1,84  | 5,94   | 0,90   | 0,70   | 0,70   | 0,76  | 0,70  | 7,34  |
| MgO                                 | 0,49            | 0,66  | 1,05  | 0,30   | 0,74  | 0,41   | 1,10   | 0,98   | 0,90   | 0,46  | 0,59  | 0,90  |
| Na <sub>2</sub> O                   | 1,53            | 1,67  | 1,60  | 1,56   | 1,85  | 3,00   | 1,72   | 1,74   | 1,60   | 2,04  | 2,68  | 2,46  |
| K <sub>2</sub> O                    | 3,01            | 1,86  | 1,53  | 3,19   | 2,90  | 2,65   | 2,66   | 2,62   | 2,58   | 2,14  | 1,82  | 2,04  |
| H <sub>2</sub> O <sup>+</sup>       | 3,33            | 3,86  | 5,14  | 3,22   | 2,83  | 2,60   | 3,49   | 5,35   | 2,22   | 4,57  | 6,24  | 2,30  |
| H <sub>2</sub> O <sup>-</sup>       | 1,34            | 3,14  | 2,29  | 1,24   | 1,79  | 2,39   | 2,17   | 1,62   | 1,70   | 2,87  | 3,36  | 2,58  |
| CO <sub>2</sub>                     | None            | 4,50  | None  | None   | 0,20  | None   | None   | None   | None   | None  | None  | 5,70  |
| C                                   | —               | None  | —     | —      | None  | —      | —      | —      | —      | —     | —     | 0,16  |
| P <sub>2</sub> O <sub>5</sub>       | 0,02            | 0,09  | 0,05  | 0,02   | 0,03  | 1,50   | 0,10   | —      | 0,02   | 0,03  | —     | None  |
| BaO                                 | 0,10            | 0,03  | 0,138 | 0,86   | 0,31  | 0,11   | 0,08   | 0,052  | 0,66   | 0,04  | 0,03  | 0,03  |
| SrO                                 | 0,34            | 0,086 | 0,46  | 0,35   | 0,26  | 0,47   | 0,26   | 0,18   | 0,24   | 0,16  | 0,10  | 0,10  |
| SO <sub>2</sub>                     | —               | —     | 0,41  | —      | —     | —      | 0,06   | None   | None   | None  | 0,02  | 0,35  |
| Total                               | 101,01          | 99,65 | 98,90 | 100,67 | 99,71 | 100,03 | 100,15 | 100,74 | 100,26 | 99,23 | 99,25 | 99,60 |
| Recalculated to element composition |                 |       |       |        |       |        |        |        |        |       |       |       |
| Ti                                  | 0,11            | 0,16  | 0,13  | 0,14   | 0,18  | 0,13   | 0,19   | 0,19   | 0,15   | 0,14  | 0,13  | 0,16  |
| Fe                                  | 2,50            | 3,42  | 3,83  | 2,28   | 3,21  | 2,41   | 2,98   | 2,65   | 1,98   | 1,33  | 2,29  | 1,86  |
| Mn                                  | 23,67           | 19,11 | 30,07 | 23,58  | 22,11 | 16,50  | 20,29  | 15,35  | 25,53  | 23,14 | 25,60 | 14,54 |
| P                                   | 0,008           | 0,04  | 0,02  | 0,008  | 0,013 | 0,66*  | 0,04   | None   | 0,008  | 0,014 | None  | None  |
| Ba                                  | 0,09            | 0,028 | 0,124 | 0,0777 | 0,028 | 0,10   | 0,07   | 0,46   | 0,59   | 0,036 | 0,026 | 0,027 |
| Sr                                  | 0,29            | 0,073 | 0,39  | 0,30   | 0,22  | 0,40   | 0,22   | 0,15   | 0,20   | 0,13  | 0,084 | 0,08  |

TABLE 11. Trace Element Content in Oxidized Manganese Ores, in 10<sup>-4</sup>%

| Ele-<br>ment | Analysis number |    |    |    |    |     |      |       |      |     |     |     |
|--------------|-----------------|----|----|----|----|-----|------|-------|------|-----|-----|-----|
|              | 1               | 2  | 3  | 4  | 5  | 6   | 7    | 8     | 9    | 10  | 11  | 12  |
| Co           | 64              | 3* | 72 | 53 | —  | 100 | 1325 | 1389  | 1262 | 515 | 979 | 350 |
| Ni           | 63              | 16 | 28 | 57 | 43 | 30  | 153  | 196   | <10  | <10 | <10 | <14 |
| V            | 30              | 30 | 40 | 20 | —  | 40  | —    | —     | —    | —   | —   | —   |
| Cr           | 10              | 10 | 10 | 10 | —  | 10  | —    | —     | —    | —   | —   | —   |
| Cu           | 74              | 15 | 1* | 25 | 29 | 100 | 10   | 151   | 114  | <10 | <10 | <10 |
| Pb           | 1*              | 30 | 1* | 3* | 23 | 289 | 125  | 1002* | 291  | 109 | 111 | 110 |
| Zn           | 58              | 22 | 38 | 49 | 46 | 60  | 260  | 282   | 183  | 156 | 202 | 182 |

Average Ti, Fe, Mn, P(%) and trace element (10<sup>-4</sup>%) content in oxidized Mn-ores (Compare with data in Tables 10 and 11)

|      |      |       |       |     |    |    |    |    |     |     |      |      |
|------|------|-------|-------|-----|----|----|----|----|-----|-----|------|------|
| Ti   | Fe   | Mn    | P     | Co  | Ni | V  | Cr | Cu | Pb  | Zn  | Sr   | Ba   |
| 0,15 | 2,59 | 21,62 | 0,013 | 555 | 52 | 28 | 10 | 49 | 136 | 128 | 2120 | 1380 |

TABLE 12. Average Element Content in Rocks and Manganese Ores, in 10<sup>-4</sup>%

| Components                         | Co  | Ni | Cu | Pb  | Zn  | Sr   | Ba   |
|------------------------------------|-----|----|----|-----|-----|------|------|
| Carbonate ore                      | 24  | 29 | 25 | 68  | 121 | 450  | 411  |
| Oxidized ore                       | 555 | 52 | 49 | 136 | 128 | 2120 | 1380 |
| Ore of concretion                  | 13  | 33 | 23 | 17  | 56  | 376  | 494  |
| Enclosing rocks                    | 18  | 48 | 20 | 10  | 63  | 346  | 571  |
| Clarke values in sedimentary rocks | 20  | 95 | 57 | 20  | 80  | 450  | 800  |

tures, partially coloring them black. Dombrovskaya identified todorokite, cryptomelane, birnessite and pyrolusite among the ore minerals. Todorokite and cryptomelane are the main ore minerals of the interior, dense subshells of the kariolites, while birnessite is more typical of the exterior layers. Pyrolusite, although its presence established long ago, is less common. It forms bristle- and needle-like growth along the cavity walls and leached organic remains. Occasionally, newly formed opal and heulandite-type zeolites also appear in the same cavities. Dombrovskaya thought that todorokite was the earliest ore mineral and it was replaced by cryptomelane. Birnessite formed from todorokite and cryptomelane. Pyrolusite is the latest ore mineral.

The chemical composition of the oxide ore and data on their trace elements is given in Tables 10 and 11. Samples from the dense ore subshells were used. Table 10 shows that the Mn-metal content in these rocks reaches 30%; most of it occurring as MnO<sub>2</sub>. The MnO content is c. 2% on the average. Typically, MnO occurs in those ore types that totally lack CO<sub>2</sub> (Table 10, analyses No. 1, 2, 3, 6-11): Mn<sup>2+</sup> is not tied to carbonates and enters oxidized Mn-minerals. Relatively high CO<sub>2</sub> content is shown only in analyses No. 2 and 12 (4.5% and 4.7%, respectively). In these samples the CaO content also increases to 7.97% and 7.34%, respectively, indicative of the presence of calcite. Analysis No. 6 produced somewhat unusual results: high (5.94%) CaO content and low (0.61%) CO<sub>2</sub> concentration. Such a discrepancy may be explainable by the fact that Ca is partially tied to P, the concentration of which in this sample is much higher than the usual value. In addition, heulandite inclusions have also been found in the ore matter of that sample. This increased not only the Ca-content, but also the Na-content to 3%; compared with 1.85% that was the average Na value in the oxide ores.

The Fe-content in the oxide ores was low, 2.59% on the average. This is the same value found in the carbonate ores; only a few tenths of a percent higher than its value in rocks that enclose kariolites and values found in kariolite cores. When separate iron shells occur in kariolites, their Fe content increases to 16% and the Mn-content increases from a few tenths of one percent to several percents.

A greater consistency characterizes the Ti concentration (range: 0.11-0.19%), with an average of 0.15%. This value corresponds to values, found in carbonate ores. P was distri-

buted unevenly, with a range between zero and several tenths of one percent. The average was 0.15%; somewhat lower than in carbonate ores. This uneven distribution is generally typical both of oxide and carbonate ores.

In identifying trace element distribution patterns in the ores, their concentration in carbonate and oxide ores was compared in kariolite nuclei and in rocks that enclose them (Table 12).

Based on this information, our conclusions are the following: in the ore-free rocks of the productive lithosome and sandy nuclei of kariolites trace elements did not display any concentration increase. A trend toward increase starts in carbonate ores; more clearly in their oxidized varieties. In comparison with the enclosing rocks, the carbonate ores contain six times as much Pb, twice as much Zn and about the same amount of Co, Cu, Sr, Ba. A very minor increase was found in the Co, Cu, and Pb content of oxidized ores in contrast with carbonate ores, and a sharply increased Sr and Ba content.

This pattern of trace element distribution is relatively easily explainable by the accumulation of Pb and Zn at the carbonate barrier, with  $\text{CaCO}_3$  coprecipitation [5] occurring. At the sulfate barrier Sr, Ba, and Pb accumulate. Consequently during the oxidizing process through the reaction  $\text{FeS}_2 + \text{O}_2 \rightarrow \text{Fe}^{2+} + \text{SO}_4^{2-}$ . An excess of sulfate ion concentration occurs on the boundary of the oxidizing concretions that include pyrite inclusions. In conjunction with Ba and Sr that are of background levels, low-solubility sulfate compounds form with these elements. Finally, Co, Ni and Cu are inclined to be adsorbed on newly formed Mn and Fe-hydroxide gels that formed in the moment when the carbonate-Mn concretions became oxidized.

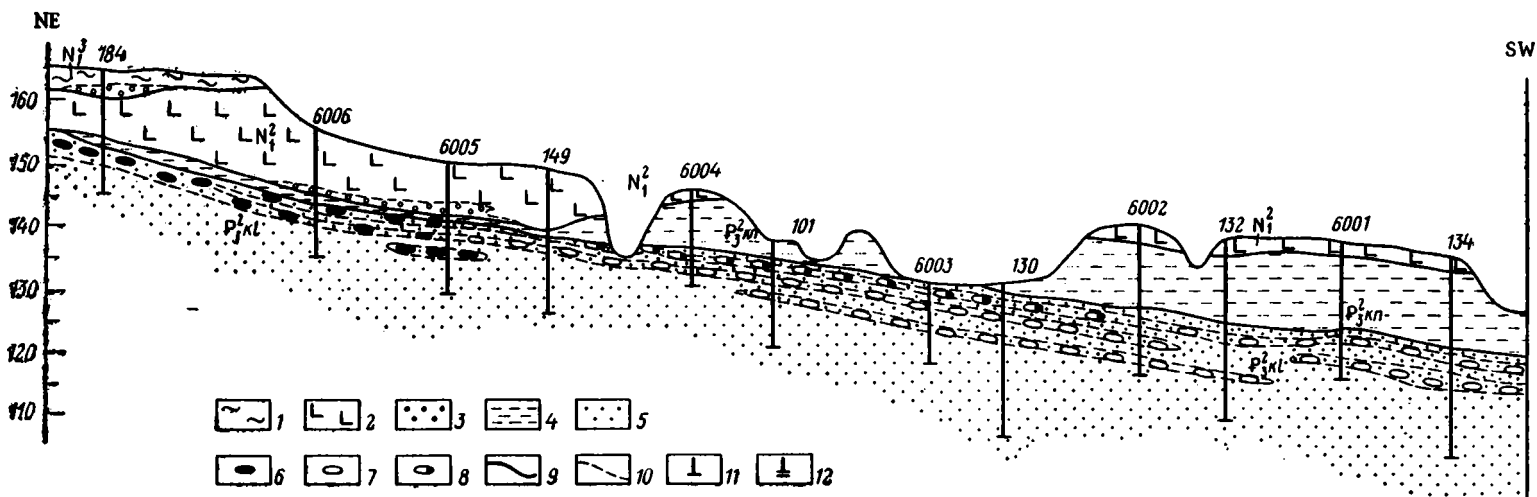
As shown above, a continuous sequence of altered carbonate ore varieties exist in the oxide ores in the studied ore deposits. The original carbonate concretions formed around specific Mn-carbonate centers. In a given instance, matter included in the concretion had migrated toward the center during concretion growth. Kariolites evolved differently. These are composed of Mn-oxides and developed through oxidation of carbonate concretions; they were derived from those concretions. During oxidation, ore compounds migrated from the concretion center toward the periphery. This resulted in the transformation of the shape and structure of the initial concretions.

Apparently, kariolite formation started with Mn-carbonate concretions that, without doubt, contained minor admixtures of iron sulfides (as shown by ochre-bearing inclusions in the concretions) that first became oxidized. Due to local acidity increase in the concretions that increased permeability and led to mobile  $\text{Fe}^{2+}$ ,  $\text{Mn}^{2+}$ , and  $\text{Ca}^{2+}$  ions, iron was able to migrate beyond the limits of the oxidation zone (the surface of the concretions). At that interface, the acidity of the medium sharply declines and  $\text{Fe}^{2+}$  was oxidized to  $\text{Fe}(\text{OH})_3$ . A primary iron shell formed. Such shells may form only when strongly oxidizing conditions are present. At the same time, conditions may be favorable for the formation, under oxidizing conditions, of sulfate from the pyrite's S. Fe would enter the surrounding solution as mobile, migrating  $\text{Fe}^{2+}$ . No iron shell would form under such conditions. Under these circumstances it obviously is not always possible for iron rich nuclei to form in the kariolites.

Oxidation of  $\text{Mn}^{2+}$  is only possible when the concretion contains no sulfide admixture whatsoever. Such admixtures would play a stabilizing role for  $\text{Mn}^{2+}$ . Oxidation of  $\text{Mn}^{2+}$  occurred in several stages. Initially, relatively low- $\text{MnO}_2$  oxides form (birnessite), but with increasing oxidation capacity of the medium,  $\text{MnO}_2$  becomes predominant and forms a dense todorokite-cryptomelane shell close to the concretion nucleus. This dense shell reduces  $\text{O}_2$ -permeability inside the shell and hinders  $\text{Mn}^{2+}$  in leaving the nucleus. Permeability in the shell, however, is not uniform. This is typical of the mineral-forming process in anisotropic media.

The secondary character of the Mangyshlak oxide ores is also confirmed by their spatial distribution pattern. The kariolite zone formed in a zone of the producing ore that is closest to the Karatu meganticline (Fig. 3). In this zone the producing bed is overlain, across an erosional unconformity, by deposits of the Upper Miocene Karagansk and Konksk stages. To the SW, depending on the depth of burial, oxide ores in the Chakyrkansky syncline gradually alternate laterally with carbonate ores across a zone of partially oxidized carbonate ores. In the carbonate ore zone the producing unit is conformably overlain by clays of the Kendzhalinsk Formation isolating it from the Middle Miocene transgressive onlap sequence.





The proximity of the oxide ore development area to the Karatau meganticline may be explained, first, by the fault between the meganticline and the Chakyransk syncline. In the zone along the fault carbonate ore oxidation occurs more intensively, due to the higher permeability. Second, at the end of the Lower Miocene, start of a general differential uplift led to denudations and partial removal of the earlier deposited sediments. The erosion depth increased toward the uplift and, as the result, the productive ore nearest to Karatau in pre-Karagansk times was exposed in the land surface and partially removed by erosion. At the time when the tectonic movements changed their directions faults also became active.

It is thought that oxidation of the carbonate ores also continued in the pre-Karagansk times. The second stage of this process took place during the Quaternary. During this time, gullying deeply dissected the ore deposit area and the ores again were subjected to hypergenetic alterations.

As the producing ore units became buried, a gradual Mn-decrease took place in the carbonate concretions in the Chakyransk syncline area. Low-Mn and, further, purely calcite concretions occur with increased pyrite content along the distal flanks of the ore deposit. Thus, there is a gradual, lateral diminution of initially Mn-rich concretions to low-Mn, later calcitic varieties. There is also a tendency toward increased iron content in the concretions.

Two major concepts deal with the genesis of the Mangyshlak deposit: a sedimentary and volcano-sedimentary theory. The first originated with Betekhtin [2] and was later developed by Tikhomirova [16], Strakhov and others [15], Mnushkin [7] and Berdichevskaya and others [1]. They thought that the Mn-compounds came into the basin from the weathering horizons of adjacent land areas. The related source rocks were thought to have been somewhat enriched in Mn (several multiples of the Clarke value). The manganese was transported into the drainage basin in solution (according to Strakhov, as bivalent bicarbonate), along with the migration of detrital sediments. The transport of ore solutions and terrigenous suspensions occurred in streams. The ore solutions were shed into an  $O_2$ -rich basin where they quickly became oxidized. Mn-hydroxide gels also formed at the same time and these precipitated into the sediments of the inner shelf zone. This primary ore sediment became Mn-rich during diagenesis. If the reduction process progressed further, the manganite became Mn-carbonate. Intensive redistribution of the ore component occurred during diagenesis and this led to concretion development.

During the Oligocene land occupied the area of the Karatau meganticline and this was thought to be the source region for the Mn compounds of the Mangyshlak ore deposit. During the time when the ore producing unit of the rock sequence has accumulated, the mostly terrigenous lower Cretaceous formations have undergone erosion. These occasionally, also contained limey rocks, but mostly sandstones with quartz, feldspar and glauconitic components, and clays. Individual intervals of the section contain limestone and marl beds. According to Strakhov, the sandstones, especially their limey varieties, contain slightly increased amounts (0.2-0.7%; 0.4% on average) of Mn and this made them candidates for consideration as ore-source rocks. This conclusion is objectionable. First, increased Mn content occurs mostly in the limey sandstones; in those very rock types that are relatively scarce. Consequently, the total Mn-supply available from the Lower Cretaceous beds is not that great. Second, during the first half of the Oligocene, the area of the eroded land and drainage areas was of limited size. The Karatau islands would have been unable to supply enough manganese to the marine basin that would account for the ore deposit. Third, no indications of manganese admixture have been found in rocks above and below the producing ore unit, or in deposits that are laterally correlatable with them at some distance from the ore deposit. Furthermore, within the producing unit the sandy-silty matter contains Mn in regional Clarke concentrations outside the ore concretions. This means that during the accumulation of Oligocene beds, no terrigenous material, enriched in manganese, was transported in larger quantities to result in formation of the manganese ore deposits. Fourth, the  $O_2$ -saturation of the river waters; the oxidized state of the depositional medium, are always higher than of any marine basin. Therefore, the fluvial deltaic zone may not be an oxygen barrier to water-soluble Mn. In addition, Mn-solubility is very low in fresh water.

The second theory was offered by Druzhinin and Galaktionov [3, 6] who applied assumptions by Dzotsenidze [4], admitting the possibility that certain manganese deposits of the Oligocene Province are of volcano-sedimentary origin. The main argument on behalf of this

concept is the position of the deposits in fault zones. Faults may have provided permeability for ore matter transport into the early Oligocene marine basin from deep endogenic sources. The assumption that the deposit occurs in an area of higher permeability does not necessarily mean a tie to volcanic ore forming processes. The hypothesis on Oligocene hydrotherms should be supported by more substantial reasoning, but such does not exist. Furthermore, certain geological and geochemical premises cast doubt on this assumption. Above all, hydrothermal activity and even more, hydrotherma of endogenic sources regionally or in time are connected to volcanic activity in its effusive or explosive varieties. No volcanic rocks have been found in Eocene and Oligocene beds in the Mangyshlak and adjacent areas. It is also difficult to assume that hydrothermal solutions exist that contain only Mn. Actual volcano-sedimentary manganese deposits have a well-defined geochemical habit. They are characterized by a close relationship between Mn and silica, a great variety in the Mn/Fe ratio values in the ores, the presence of even Mn-bearing iron ores in certain deposits, along with monometallic Mn-ores and their iron-bearing varieties, as well as strong enrichment of the ore in individual trace elements. None of these features are present in the Mangyshlak deposit. Therefore, the theory of the ore's volcanic origin is inappropriate in this deposit.

The two genetic theories therefore do not satisfactorily explain the origins of the Mangyshlak ore deposit. New ways must be found in deciding this problem, to be discussed in the following publication.

Analysis of the discussed geological data leads us to the following conclusions:

1. The deposit is found in sediments which carry no signs of having been influenced by Mn. Such deposits include sandy rocks, directly surrounding the rock and clays, found beyond the productive unit. Furthermore, the Mn content tends to decrease in the clays with decreasing distances from the deposit.
2. Clays of the Maikop Series typically contain almost no carbonate and therefore contain small concentrations of Ca. They invariably include organic matter and Fe-sulfides.
3. The Mn-ores are associated only with sandy deposits that form a small body on the southern limb of the Karatau meganticline, cut by fractures. It is thought that activation of the faults and the consequent increase in permeability occurred in two peak stages: the first at the beginning of the Oligocene (basin formation with sharply differentiated bottom relief) and a second, that followed immediately the deposition of the Maikop Series. (At a time when the directions of the oscillating tectonic movements changed during pre-Karagansk stages of the region's development.)
4. Strakhov's views were supported by the fact that only Mn-carbonate ores are the primary formations in the deposit. This is based on geological and geochemical data. For the first time, the kariolite development process is discussed. Kariolites form in the oxidation process of carbonate ores.
5. As the productive unit is buried deeper, the trend increases toward Mn-depletion in the carbonate concretions. At the same time, the Ca-carbonates play a greatly increased role and iron concretions become somewhat more important.

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#### GENERALIZED CLASSIFICATION OF COAL-BEARING ROCKS AND COAL

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UDC 553.94

The results are presented of detailed petrophysical studies of the sediments of coal deposits and coal basins, yielding a list of petrophysical types (petrotypes) identified in the cross section of parametric wells by geological and geophysical methods. On the basis of these petrotypes and their descriptions according to the grain size and optimal composition, a generalized classification of rocks and coals of coal-bearing formations has been constructed.

The lithology of coal-bearing sediments is the foundation of studies of the main features of coal deposits and basins: tectonics, stratigraphy, physical and mechanical properties, strength and composition of rocks, morphology of coal seams, gas contents of coal deposits, sudden bursts in the mines, and other aspects.

It is essential for coal mining to define the lithologic characteristics of each seam and study its physical and granulometric composition, the type and composition of cement, the contents of organic matter, etc. This information is important for the study of the

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All-Union Scientific-Research Institute of Geology and Geophysics, Moscow. Translated from *Litologiya i Poleznye Iskopaemye*, No. 1, pp. 80-93, January-February, 1987. Original article submitted September 12, 1985.

TABLE 1. Generalized Classification of Rocks and Coals of Coal-Bearing Formations

| Petro-<br>type<br>number | Stage of rock alteration                          |                                                   |                                                                  |                                                                  | Fragment<br>size, mm | Optimal composition of cemented<br>rock, % |                            |                   |                   |
|--------------------------|---------------------------------------------------|---------------------------------------------------|------------------------------------------------------------------|------------------------------------------------------------------|----------------------|--------------------------------------------|----------------------------|-------------------|-------------------|
|                          | syngensis                                         | diagenesis                                        | epigenesis (catagenesis)                                         | metagenesis                                                      |                      | clay<br>cement                             | carbon-<br>ate ce-<br>ment | clastic<br>matter | organic<br>matter |
| I                        | Pebblestone                                       | Pebblestone                                       | Conglomerate                                                     | Conglomerate                                                     | $>1,0$               | 0—5                                        | 0—10                       | 90—100            | —                 |
| II                       | Carbonaceous loose<br>coarse-grained sand         | Carbonaceous dense<br>coarse-grained sand         | Coarse-grained sandstone<br>with carbonaceous ce-<br>ment        | Coarse-grained sandstone<br>with carbonaceous ce-<br>ment        | 0,5—1,0              | 0—7                                        | 10—21                      | 79—90             | —                 |
| III                      | Clayey coarse-grained<br>loose sand               | Clayey coarse-grained<br>dense sand               | Coarse-grained sandstone<br>with clay cement                     | Coarse-grained sandstone<br>with clay cement                     | 0,5—1,0              | 0—12                                       | 0—10                       | 83—95             | —                 |
| IV                       | Carbonate medium-<br>grained loose sand           | Carbonate medium-<br>grained dense sand           | Medium-grained sand-<br>stone with carbonate<br>cement           | Medium-grained sand-<br>stone with carbonate<br>cement           | 0,25—0,5             | 0—9                                        | 25—41                      | 59—75             | —                 |
| V                        | Carbonaceous-clay<br>medium-grained<br>loose sand | Carbonaceous-clay<br>medium-grained<br>dense sand | Medium-grained sand-<br>stone with carbonace-<br>ous-clay cement | Medium-grained sand-<br>stone with carbonace-<br>ous-clay cement | 0,25—0,5             | 0—16                                       | 10—25                      | 66—83             | —                 |
| VI                       | Clayey medium-<br>grained loose sand              | Clayey medium-<br>grained dense sand              | Medium-grained sand-<br>stone with clay cement                   | Medium-grained sand-<br>stone with clay cement                   | 0,25—0,5             | 7—21                                       | 0—10                       | 74—88             | —                 |
| VII                      | Carbonate-clay medi-<br>um-grained loose<br>sand  | Carbonate-clay medi-<br>um-grained dense<br>sand  | Fine-grained sandstone<br>with carbonaceous-clay<br>cement       | Fine-grained sandstone<br>with carbonaceous-clay<br>cement       | 0,1—0,25             | 0—21                                       | 25—50                      | 41—66             | —                 |
| VIII                     | Clay-carbonaceous<br>fine-grained loose<br>sand   | Clay-carbonaceous<br>fine-grained dense<br>sand   | Fine-grained sandstone<br>with clay-carbonaceous<br>cement       | Fine-grained sandstone<br>with clay-carbonaceous<br>cement       | 0,1—0,25             | 9—28                                       | 10—25                      | 54—74             | —                 |
| IX                       | Fine-grained clayey<br>loose sand                 | Fine-grained clayey<br>dense sand                 | Fine-grained sandstone<br>with clay cement                       | Fine-grained sandstone<br>with clay cement                       | 0,1—0,25             | 16—32                                      | 0—10                       | 62—79             | —                 |
| X                        | Silt-carbonate-clay<br>ooze                       | Mixed silt-carbonate-<br>clay rock                | Mixed silt-carbonate-<br>clay rock                               | Silt-carbonate-clay<br>schist                                    | 0,05—0,1             | 9—38                                       | 25—50                      | 25—54             | —                 |
| XI                       | Silt-clay-carbonace-<br>ous ooze                  | Clay-carbonaceous<br>silt                         | Siltstone with clay-car-<br>bonaceous cement                     | Silt-clay-carbonaceous<br>schist                                 | 0,05—0,1             | 21—45                                      | 10—25                      | 37—62             | —                 |
| XII                      | Silt-clay ooze                                    | Clayey silt                                       | Siltstone with clay ce-<br>ment                                  | Silt-clayey schist                                               | 0,05—0,1             | 28—50                                      | 0—10                       | 45—68             | —                 |
| XIII                     | Carbonate-clay-silt<br>ooze                       | Mixed carbonate-clay-<br>silt rock                | Mixed carbonate-clay-<br>silt rock                               | Carbonate-clay-silt<br>schist                                    | 0,01—0,05            | 25—58                                      | 25—50                      | 8—37              | —                 |
| XIV                      | Clay-silt-carbonace-<br>ous ooze                  | Clay-silt-carbonace-<br>mixed rock                | Clay-silt-carbonaceous<br>mixed rock                             | Clay-silt-carbonaceous<br>schist                                 | 0,01—0,05            | 38—69                                      | 10—25                      | 17—45             | —                 |
| XV                       | Silty ooze                                        | Silty clay                                        | Silty argillite                                                  | Clay-silty schist                                                | 0,01—0,05            | 45—75                                      | 0—10                       | 21—50             | —                 |
| XVI                      | Clay-carbonate ooze                               | Carbonate clay                                    | Carbonate argillite                                              | Clay-carbonate schist                                            | $<0,01$              | 42—75                                      | 25—50                      | 0—17              | —                 |
| XVII                     | Clay-carbonaceous<br>ooze                         | Carbonaceous clay                                 | Carbonaceous argillite                                           | Clay-carbonaceous schist                                         | $<0,01$              | 58—90                                      | 10—25                      | 0—21              | —                 |
| XVIII                    | Clayey ooze                                       | Clay                                              | Clayey argillite                                                 | Clayey schist                                                    | $<0,01$              | 69—100                                     | 0—10                       | 0—25              | —                 |
| XIX                      | Sandstone nodules                                 | Sandy carbonate rock<br>(nodules)                 | Sandy carbonate rock<br>(nodules)                                | Sandy carbonate rock<br>(nodules)                                | $<0,01—0,25$         | 0—9                                        | 50—70                      | 30—50             | —                 |
| XX                       | Silty nodules                                     | Silty carbonate rock<br>(nodules)                 | Silty carbonate rock<br>(nodules)                                | Silty carbonate rock<br>(nodules)                                | 0,05—0,1             | 0—25                                       | 50—75                      | 12—41             | —                 |

|        |                              |                                      |                                      |                                      |           |       |        |       |       |
|--------|------------------------------|--------------------------------------|--------------------------------------|--------------------------------------|-----------|-------|--------|-------|-------|
| XXI    | Clayey-silt nodules          | Clayey-silt carbonate rock (nodules) | Clayey-silt carbonate rock (nodules) | Clayey-silt carbonate rock (nodules) | 0,01—0,05 | 13—42 | 50—75  | 0—25  | —     |
| XXII   | Clayey nodules               | Clayey carbonate rock (nodules)      | Clayey carbonate rock (nodules)      | Clayey carbonate rock (nodules)      | <0,01     | 25—50 | 50—75  | 0—8   | —     |
| XXIII  | Nodules                      | Carbonate rocks (nodules)            | Carbonate rocks (nodules)            | Carbonate rocks (nodules)            |           | 0—25  | 75—100 | 0—25  | —     |
| XXIV   | Calcareous-sandy ooze        | Sandy limestone                      | Sandy limestone                      | Sandy limestone                      | 0,1—0,25  | 0—9   | 50—70  | 30—50 | —     |
| XXV    | Calcareous-silty ooze        | Silty limestone                      | Silty limestone                      | Silty limestone                      | 0,05—0,1  | 0—25  | 50—75  | 12—41 | —     |
| XXVI   | Calcareous-clayey-silty ooze | Clayey-silty limestone               | Clayey-silty limestone               | Clayey-silty limestone               | 0,01—0,05 | 13—42 | 50—75  | 0—25  | —     |
| XXVII  | Calcareous ooze              | Clayey limestone                     | Clayey limestone                     | Clayey limestone                     | <0,01     | 25—50 | 50—75  | 0—8   | —     |
| XXVIII | Calcareous ooze              | Limestone                            | Limestone                            | Limestone                            |           | 0—25  | 75—100 | 0—25  | —     |
| XXIX   | Low-humus ooze               | Low-coaly clay                       | Low-coaly argillite                  | Low-coaly clayey schist              | <0,01     | 80—90 | 0—10   | 0—10  | 10—20 |
| XXX    | Medium-humus ooze            | Medium-coaly clay                    | Medium-coaly argillite               | Medium-coaly clayey schist           | <0,01     | 65—80 | 0—10   | 0—10  | 20—35 |
| XXXI   | High-humus ooze              | High-coaly clay                      | High-coaly argillite                 | High-coaly clayey schist             | <0,01     | 50—65 | 0—7    | 0—7   | 35—50 |
| XXXII  | High-ash peat                | High-ash brown coal                  | High-ash bituminous coal             | High-ash anthracite                  | —         | 30—50 | 0—5    | 0—5   | 50—70 |
| XXXIII | Medium-ash peat              | Medium-ash brown coal                | Medium-ash bituminous coal           | Medium-ash anthracite                | —         | 15—30 | 0—3    | 0—3   | 70—85 |
| XXXIV  | Low-ash peat                 | Low-ash brown coal                   | Low-ash bituminous coal              | Low-ash anthracite                   | —         | 5—15  | 0—1    | 0—1   | >85   |

| Petrotype number | Rock alteration stage |            |            |             | Petrotype number | Rock alteration stage |            |            |             |
|------------------|-----------------------|------------|------------|-------------|------------------|-----------------------|------------|------------|-------------|
|                  | syngenesis            | diagenesis | epigenesis | metagenesis |                  | syngenesis            | diagenesis | epigenesis | metagenesis |
| I                |                       |            |            |             | VIII             |                       |            |            |             |
| II               |                       |            |            |             | IX               |                       |            |            |             |
| III              |                       |            |            |             | X                |                       |            |            |             |
| IV               |                       |            |            |             | XI               |                       |            |            |             |
| V                |                       |            |            |             | XII              |                       |            |            |             |
| VI               |                       |            |            |             | XIII             |                       |            |            |             |
| VII              |                       |            |            |             | XIV              |                       |            |            |             |
| XV               |                       |            |            |             | XXV              |                       |            |            |             |
| XVI              |                       |            |            |             | XXVI             |                       |            |            |             |
| XVII             |                       |            |            |             | XXVII            |                       |            |            |             |
| XVIII            |                       |            |            |             | XXVIII           |                       |            |            |             |
| XIX              |                       |            |            |             | XXIX             |                       |            |            |             |
| XX               |                       |            |            |             | XXX              |                       |            |            |             |
| XXI              |                       |            |            |             | XXXI             |                       |            |            |             |
| XXII             |                       |            |            |             | XXXII            |                       |            |            |             |
| XXIII            |                       |            |            |             | XXXIII           |                       |            |            |             |
| XXIV             |                       |            |            |             | XXXIV            |                       |            |            |             |

Fig. 1. Symbolic notations of petrotypes of the generalized classification of coal-bearing formations. For petrotype name, see Table 1.

roofs and floors of coal seams, where these properties must be determined in each layer of the thickness of 5 cm and more. Detailed descriptions of rock lithology are crucial for reliable reconnaissance of coal deposits.

Lithological investigations of coal deposits are largely based on visual descriptions of cores from bore holes. Only a small proportion of specimens, usually from the strongest rocks, are subjected to laboratory analysis, because softer rocks are often crushed and washed out in the course of drilling.

In addition, such analyses are laborious and expensive; only a small proportion of specimens are thus investigated, which are not representative of the regular variations of rocks in the cross section of the bore hole.

In practice, the lithology of most coal-bearing rocks is described on the basis of visual inspections in terms of the size of clastic material, virtually ignoring the contents of the main admixtures of clay and clastic particles. Huge amounts of cores are extracted with the current high speeds of drilling, even if partially, and geologists are incapable of documenting fully this material even by visual inspection.

The absence of a unified classification is a major drawback of the existing methods of lithologic studies of rocks. "Local" classifications are used in different basins, which,

| Petro-<br>type no. | C <sub>clas</sub><br>% |    |    | C <sub>cl</sub><br>% |    |    | C <sub>cb</sub><br>% |    |    | K <sub>p</sub><br>% | $\sigma$ |     |     |     |     | $\rho_p$<br>g/cm <sup>3</sup> | $v_p$<br>km/sec | $\Delta J_\gamma$<br>rel. un |     |     |
|--------------------|------------------------|----|----|----------------------|----|----|----------------------|----|----|---------------------|----------|-----|-----|-----|-----|-------------------------------|-----------------|------------------------------|-----|-----|
|                    | 0                      | 40 | 80 | 0                    | 40 | 80 | 0                    | 40 | 80 | 2                   | 6        | 265 | 285 | 305 | 325 | 345                           | 100             | 300                          | 0.2 | 0.6 |
| I                  |                        |    |    |                      |    |    |                      |    |    |                     |          |     |     |     |     |                               |                 |                              |     |     |
| II                 |                        |    |    |                      |    |    |                      |    |    |                     |          |     |     |     |     |                               |                 |                              |     |     |
| III                |                        |    |    |                      |    |    |                      |    |    |                     |          |     |     |     |     |                               |                 |                              |     |     |
| IV                 |                        |    |    |                      |    |    |                      |    |    |                     |          |     |     |     |     |                               |                 |                              |     |     |
| V                  |                        |    |    |                      |    |    |                      |    |    |                     |          |     |     |     |     |                               |                 |                              |     |     |
| VI                 |                        |    |    |                      |    |    |                      |    |    |                     |          |     |     |     |     |                               |                 |                              |     |     |
| VII                |                        |    |    |                      |    |    |                      |    |    |                     |          |     |     |     |     |                               |                 |                              |     |     |
| VIII               |                        |    |    |                      |    |    |                      |    |    |                     |          |     |     |     |     |                               |                 |                              |     |     |
| IX                 |                        |    |    |                      |    |    |                      |    |    |                     |          |     |     |     |     |                               |                 |                              |     |     |
| X                  |                        |    |    |                      |    |    |                      |    |    |                     |          |     |     |     |     |                               |                 |                              |     |     |
| XI                 |                        |    |    |                      |    |    |                      |    |    |                     |          |     |     |     |     |                               |                 |                              |     |     |
| XII                |                        |    |    |                      |    |    |                      |    |    |                     |          |     |     |     |     |                               |                 |                              |     |     |
| XIII               |                        |    |    |                      |    |    |                      |    |    |                     |          |     |     |     |     |                               |                 |                              |     |     |
| XIV                |                        |    |    |                      |    |    |                      |    |    |                     |          |     |     |     |     |                               |                 |                              |     |     |
| XV                 |                        |    |    |                      |    |    |                      |    |    |                     |          |     |     |     |     |                               |                 |                              |     |     |
| XVI                |                        |    |    |                      |    |    |                      |    |    |                     |          |     |     |     |     |                               |                 |                              |     |     |
| XVII               |                        |    |    |                      |    |    |                      |    |    |                     |          |     |     |     |     |                               |                 |                              |     |     |
| XVIII              |                        |    |    |                      |    |    |                      |    |    |                     |          |     |     |     |     |                               |                 |                              |     |     |
| XIX                |                        |    |    |                      |    |    |                      |    |    |                     |          |     |     |     |     |                               |                 |                              |     |     |
| XX                 |                        |    |    |                      |    |    |                      |    |    |                     |          |     |     |     |     |                               |                 |                              |     |     |
| XXI                |                        |    |    |                      |    |    |                      |    |    |                     |          |     |     |     |     |                               |                 |                              |     |     |
| XXII               |                        |    |    |                      |    |    |                      |    |    |                     |          |     |     |     |     |                               |                 |                              |     |     |
| XXIII              |                        |    |    |                      |    |    |                      |    |    |                     |          |     |     |     |     |                               |                 |                              |     |     |

Fig. 2. An illustration of material and petrophysical characteristics of petrotypes of coal-bearing rocks (Pechora Basin, Usa deposit; epigenesis stage I (F); lithologic-geophysical stage I). C<sub>clas</sub>, C<sub>cl</sub>, and C<sub>cb</sub>) contents of clastic matter and clay and carbonate cement, respectively; K<sub>p</sub>) porosity;  $\sigma_M$ ,  $\sigma_s$ ,  $\sigma_{cl}$ ) density (mineralogic volume porosity of water-saturated rocks and of dry rocks, respectively);  $\rho_p$ ) electric conductivity; v<sub>p</sub>) velocity of P waves;  $\Delta I_\gamma$ ) relative intensity of natural gamma radiation. For petrotype names, see Table 2.

although they are often based on Shvetsov's decimal classification [6], are different and often incompatible.

It is a flaw of the current lithologic-petrographic classifications of sedimentary rocks that they all fail to take into account the degree of alteration of rocks during diagenesis, epigenesis, and metagenesis. It is well known, for example, that fine-grained sandstone with clay cement in coal deposits of stage V (D) differs in physical and mechanical properties from a similar sandstone in deposits of coal stage IX (K), although the granulometric and material composition of the rocks and the type and composition of cement are virtually the same, because the formation of authigenic minerals during epigenesis is quite limited (the same lithotype).

All this calls for creating a new rock classification free of these shortcomings, which is only possible by introducing objective geological and geophysical features characterizing rocks in a more comprehensive manner.

It is impossible, however, to divide a profile into lithologic types and determine their material compositions in terms of the physical properties alone as used in many of the geophysical methods. This is because the physical properties are determined by two groups of factors: primary (genetic) factors, associated with the material and granulometric composition of rocks, and secondary factors, reflecting the processes of rock alteration and the influence of groundwater and interstitial solutions. In a general form, there is no physical foundation for indentifying lithotypes and defining their material compositions by using geophysical methods alone.

The problem can be solved only in a special case, allowing the separation of the physical properties of rocks into two components — one associated with the composition of rocks and the other with processes altering them.



| Petro-<br>type<br>No. | SiO <sub>2</sub> | Al <sub>2</sub> O <sub>3</sub> | Fe <sub>2</sub> O <sub>3</sub> | FeO  | MnO     | MgO   | CaO  | Na <sub>2</sub> O | K <sub>2</sub> O | TiO <sub>2</sub> | P <sub>2</sub> O <sub>5</sub> | SO <sub>3</sub> | CO <sub>2</sub> | H <sub>2</sub> O |
|-----------------------|------------------|--------------------------------|--------------------------------|------|---------|-------|------|-------------------|------------------|------------------|-------------------------------|-----------------|-----------------|------------------|
|                       | 30 70            | 10 15                          | 2 4                            | 4 12 | 0.2 0.4 | 1 3 5 | 7 11 | 1 2 3             | 1 2 3            | 0.2 0.4 0.1 0.3  | 0.1 0.3                       | 0.1 0.3         | 8 16            | 1 2 3            |
| I                     |                  |                                |                                |      |         |       |      |                   |                  |                  |                               |                 |                 |                  |
| II                    |                  |                                |                                |      |         |       |      |                   |                  |                  |                               |                 |                 |                  |
| III                   |                  |                                |                                |      |         |       |      |                   |                  |                  |                               |                 |                 |                  |
| IV                    |                  |                                |                                |      |         |       |      |                   |                  |                  |                               |                 |                 |                  |
| V                     |                  |                                |                                |      |         |       |      |                   |                  |                  |                               |                 |                 |                  |
| VI                    |                  |                                |                                |      |         |       |      |                   |                  |                  |                               |                 |                 |                  |
| VII                   |                  |                                |                                |      |         |       |      |                   |                  |                  |                               |                 |                 |                  |
| VIII                  |                  |                                |                                |      |         |       |      |                   |                  |                  |                               |                 |                 |                  |
| IX                    |                  |                                |                                |      |         |       |      |                   |                  |                  |                               |                 |                 |                  |
| X                     |                  |                                |                                |      |         |       |      |                   |                  |                  |                               |                 |                 |                  |
| XI                    |                  |                                |                                |      |         |       |      |                   |                  |                  |                               |                 |                 |                  |
| XII                   |                  |                                |                                |      |         |       |      |                   |                  |                  |                               |                 |                 |                  |
| XIII                  |                  |                                |                                |      |         |       |      |                   |                  |                  |                               |                 |                 |                  |
| XIV                   |                  |                                |                                |      |         |       |      |                   |                  |                  |                               |                 |                 |                  |
| XV                    |                  |                                |                                |      |         |       |      |                   |                  |                  |                               |                 |                 |                  |
| XVI                   |                  |                                |                                |      |         |       |      |                   |                  |                  |                               |                 |                 |                  |
| XVII                  |                  |                                |                                |      |         |       |      |                   |                  |                  |                               |                 |                 |                  |
| XVIII                 |                  |                                |                                |      |         |       |      |                   |                  |                  |                               |                 |                 |                  |
| XIX                   |                  |                                |                                |      |         |       |      |                   |                  |                  |                               |                 |                 |                  |
| XX                    |                  |                                |                                |      |         |       |      |                   |                  |                  |                               |                 |                 |                  |
| XXI                   |                  |                                |                                |      |         |       |      |                   |                  |                  |                               |                 |                 |                  |
| XXII                  |                  |                                |                                |      |         |       |      |                   |                  |                  |                               |                 |                 |                  |
| XXIII                 |                  |                                |                                |      |         |       |      |                   |                  |                  |                               |                 |                 |                  |

Fig. 3. Illustration of geochemical characteristics of petrotypes of coal-bearing rocks (Pechora Basin, Usa deposit, epigenesis stage I (F); lithologic-geophysical stage I). For petrotype names, see Table 2. Contents of components given in percentage points.

Investigations of the petrophysical patterns of variation of the physical properties of coal-bearing rocks have discovered a new principle of lithologic studies which allows reducing the unsolvable general problem to special cases in which it can be solved unambiguously by means of geophysical methods of bore hole exploration. The practical implementation of this principle is based on the criterion  $K_1$ , which consists of the following. Suppose that the variation of physical parameters of similar rocks within a selected profile interval is not greater than the accuracy of their measurement by geophysical methods in the bore hole cross section. We will call such an interval of the profile a lithologic-geophysical step. An element of an area satisfying this criterion will be called a lithologic-geophysical segment. In the interval of the profile of the depth of one step and of the area of a segment, alterations of the physical properties of rocks will be associated with their composition, i.e., the different lithotypes, making it possible within these steps and segments to identify lithotypes unambiguously and to determine their composition [1-5].

The profiles of coal deposits are divided into steps by using a reference to a typical petrophysical profile of coal basins of a geosynclinal group, and into segments on the basis of regional petrophysical maps [1, 2].

Within steps and segments a second criterion,  $K_2$ , is used to define lithotypes; according to this criterion, each lithotype should differ from all others in at least one physical property and by not less than the double accuracy of its measurement as done in bore hold cross sections by geophysical methods.

With these criteria for separation of geological profiles of coal deposits into lithologic-geophysical steps, the deposit areas into lithologic-geophysical segments, and the rock within these units into lithologic types, the degree of detail of separation of profiles in terms of composition has been improved by a factor of 4 or 5 compared with the conventional geological and geophysical (well logging) methods of bore hole cross section documentation.

We proceed from the assumption coal-bearing sediments consist of three components: clastic matter, clay cement, and carbonate cement. By composition, the rocks in the profiles of the deposits usually remain invariable, while varying in their physical properties the number of times equal to the number of lithologic-geophysical steps identified in the profile. For example, in a profile of a bituminous coal deposit 1200-m thick five steps have been identified. Since petrophysical indicators are included in the characteristics of lithologic types, the degree of detail of the separation of the coal deposit profile by inclusion of these new petrophysical indicators is increased by another four to five times, so that, altogether, counting the compositional and petrophysical indicators, the degree of detail is improved by a factor of 20-25. In addition to these indicators, the characterization of a lithotype is supplemented by geochemical characteristics in terms of the main

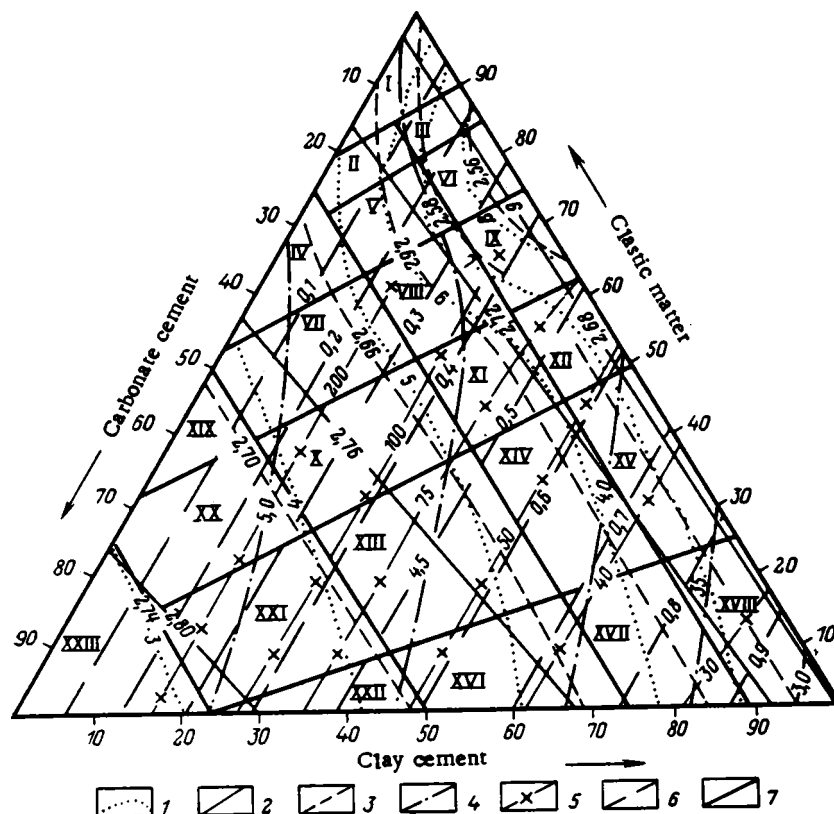


Fig. 4. An example of a chart for identification of coal-bearing rock petrotypes in bore hole sections and determination of their composition (Usa deposit, Pechora Basin, epigenetic stage VIII (F); lithologic-geophysical step I). 1) porosity; 2) mineralogic density,  $\text{g/cm}^3$ ; 3) density of water-logged rocks,  $\text{g/cm}^3$ ; 4) velocity of elastic P waves,  $\text{km/sec}$ ; 5) electric resistivity,  $\text{m}$ ; 6) intensity of natural gamma radiation, rel. units; 7) petrotype boundaries. I-XVIII) petrotype numbers (see Table 2).

oxides and elements based on laboratory analyses. A lithologic type is thus characterized by the following indicators: \* granulometric (1), compositional (3), geochemical (14), and also petrophysical (8) and epigenetic (2). This notion of a type, which differs substantially from the conventional definition commonly used by lithologists, and includes all of these indicators, will be referred to as a petrophysical type (or petrotype). A petrotype is a more comprehensive notion which characterizes rocks in various aspects and can be used in practice for a detailed investigation of rock lithology; composition; strength; deformational, structural, engineering, and physicommechanical properties; stability; and susceptibility to collapse, swelling, and rock burst hazards in the mine.

Data for rock characterization are obtained from parametric bore holes drilled in the deposits. The results of geological, petrophysical, geophysical, and petrographic studies are used to correlate the geologic characteristics with petrophysical information and to prepare working charts for determination of these indicators by geophysical methods. Once this is done, the remaining reconnaissance wells can be drilled in the deposit without a core, defining all the rock indicators by geophysical techniques [2].

On the basis of investigations in parametric bore holes in the deposits of Pechora, Donets, and Kuznetsk Basins, new rock classifications have been constructed in terms of these indicators as they apply to these basins. Unequal numbers of petrophysical types have been distinguished in the different basins: 23 in Pechora, 28 in Donets, and 23 in Kuznetsk [3-5].

\*The number of indicator is given in parentheses; there is a total of 28 indicators.

TABLE 2. Petrographic Characteristics of Coal-Bearing Rocks, Pechora Basin, Usa Deposit, Epigenesis Stage I (F), Lithologic-Geophysical Stage I

| Petrotype number | Petrotype name                                         | Petrographic characteristics |                                |                      |                                      |                               |                |                  |                |
|------------------|--------------------------------------------------------|------------------------------|--------------------------------|----------------------|--------------------------------------|-------------------------------|----------------|------------------|----------------|
|                  |                                                        | color                        | texture                        | structure            | cement                               | predominant fragment size, mm | composition, % |                  |                |
|                  |                                                        |                              |                                |                      |                                      |                               | clay cement    | carbonate cement | clastic cement |
| I                | Conglomerate                                           | Variegated                   | Psephitic, small-pebble-gravel | Massive unstratified | Film, film-interstitial              | 1,0                           | 0—5            | 0—10             | 90—100         |
| II               | Coarse-grained sandstone with carbonaceous cement      | Light gray                   | Psammitic                      | Massive              | Interstitial                         | 0,5—1,0                       | 0—7            | 10—21            | 79—90          |
| III              | Coarse-grained sandstone with clay cement              | "                            | "                              | "                    | "                                    | 0,5—1,0                       | 0—12           | 0—10             | 83—95          |
| IV               | Medium-grained sandstone with carbonate cement         | "                            | "                              | "                    | "                                    | 0,25—0,5                      | 0—9            | 25—41            | 59—75          |
| V                | Medium-grained sandstone with carbonaceous-clay cement | "                            | "                              | "                    | "                                    | 0,25—0,5                      | 0—16           | 10—25            | 66—83          |
| VI               | Medium-grained sandstone with clay cement              | Gray                         | Silt-psammitic                 | Massive stratified   | "                                    | 0,25—0,5                      | 7—21           | 0—10             | 74—88          |
| VII              | Fine-grained sandstone with carbonate-clay cement      | "                            | Psammitic                      | Massive              | Interstitial, corrosion-interstitial | 0,1—0,25                      | 0—21           | 25—50            | 41—66          |
| VIII             | Fine-grained sandstone with clay-carbonaceous cement   | Gray                         | Psammite                       | Massive              | Interstitial, basal                  | 0,1—0,25                      | 9—23           | 10—25            | 54—74          |
| IX               | Fine-grained sandstone with clay cement                | "                            | Psammitic, silt-psammitic      |                      | "                                    | 0,1—0,25                      | 16—32          | 0—10             | 62—79          |

|       |                                         |                      |                                          |                                             |                            |           |        |        |       |
|-------|-----------------------------------------|----------------------|------------------------------------------|---------------------------------------------|----------------------------|-----------|--------|--------|-------|
| X     | Mixed silt-carbonate-clay rock          | Gray                 | Pelite, silt-pelite                      | Unstratified                                | Basal-interstitial         | 0,05—0,1  | 9—38   | 25—50  | 25—54 |
| XI    | Siltstone with clay-carbonaceous cement | "                    | Silty, silty-psammitic                   | Stratified                                  | "                          | 0,05—0,1  | 21—45  | 10—25  | 37—62 |
| XII   | Siltstone with clay cement              | Gray, dark gray      | Silty                                    | "                                           | "                          | 0,05—0,1  | 28—50  | 0—10   | 45—68 |
| XIII  | Mixed carbonate-clay-silt rock          | "                    | Pelite-silty                             | Unstratified, stratified                    | Basal                      | 0,01—0,05 | 25—58  | 25—50  | 8—37  |
| XIV   | Mixed clay-silt-carbonaceous rock       | Dark gray, gray      | "                                        | Stratified                                  | "                          | 0,01—0,05 | 38—69  | 10—25  | 17—45 |
| XV    | Silty argillite                         | "                    | Pelitic                                  | "                                           | Clay-carbonate aggregate   | 0,01—0,05 | 45—75  | 0—10   | 21—50 |
| XVI   | Carbonate argillite                     | Gray                 | Pelite, combined with spherulitic        | Unstratified                                | Carbonate-clay aggregate   | 0,01      | 42—75  | 25—50  | 0—17  |
| XVII  | Carbonaceous argillite                  | Dark gray, gray      | Pelitic, less frequency spherulitic      | Unclearly stratified, tenticular-stratified | "                          | 0,01      | 58—90  | 10—25  | 0—21  |
| XVIII | Argillite                               | Dark gray            | Pelitic                                  | Fine-layered, unclearly layered             | Clay aggregate             | 0,01      | 69—100 | 0—10   | 0—25  |
| XIX   | Sandy carbonate rock (nodules)          | Gray                 | Psammitic                                | Massive, less often spotty                  | Corrosional                | 0,1—0,25  | 0—9    | 50—70  | 30—50 |
| XX    | Silty carbonate rock (nodules)          | "                    | Silty                                    | Massive                                     | "                          | 0,05—0,1  | 0—25   | 50—75  | 12—41 |
| XXI   | Clay-silty carbonate rock (nodules)     | "                    | Pelitimorphous combined with spherulitic | "                                           | Carbonate-clayey           | 0,01—0,05 | 13—42  | 50—75  | 0—25  |
| XXII  | Clayey-carbonate rock (nodules)         | Gray, yellowish-gray | Pelitimorphous                           | "                                           | Carbonate-clayey aggregate | 0,01      | 25—50  | 50—75  | 0—8   |
| XXIII | Carbonate rock (nodules)                | Gray                 | "                                        | "                                           | "                          | —         | 0—25   | 75—100 | 0—25  |

TABLE 3. Petrographic Characteristics of Coals and Coaly Rocks, Pechora Basin, Usa Deposit, Epigenesis Stage VIII (F), Lithologic-Geophysical Step I

| Petro-type number | Petrotype name         | Petrographic characteristics |                          | Texture-structural features       | Composition, wt. % |                |                              |          |             |                |
|-------------------|------------------------|------------------------------|--------------------------|-----------------------------------|--------------------|----------------|------------------------------|----------|-------------|----------------|
|                   |                        | color                        | brilliance               |                                   | organic matter     | mineral matter | including mineral impurities |          |             |                |
|                   |                        |                              |                          |                                   |                    |                | clay matter                  | sulfides | carbo-nates | clastic matter |
| XXIX              | Low-coaly argillite    | Dark gray                    | Dull                     | Phytopelitimorphous-layered       | 10—20              | 80—80          | 85—100                       | 0—8      | 0—1         | 0—6            |
| XXX               | Medium-coaly argillite | »                            | »                        | »                                 | 21—35              | 65—79          | 80—100                       | 0—6      | 0—6         | 0—6            |
| XXXI              | High-coaly argillite   | Black                        | »                        | Pelitimorphous-layered            | 35—50              | 50—64          | 70—100                       | 0—8      | 0—16        | 0—8            |
| XXXII             | High-ash coal          | Dark brown                   | »                        | Lineated striated homo-geneous    | 51—70              | 30—49          | 70—100                       | 0—10     | 0—15        | 0—15           |
| XXXIII            | Medium ash coal        | Black                        | Semibrilliant, brilliant | Striated                          | 71—85              | 15—29          | 70—100                       | 0—10     | 0—20        | 0—20           |
| XXXIV             | Low ash                | »                            | »                        | Striated, less often homo-geneous | 85                 | 15             | 70—100                       | 0—10     | 0—30        | 0—30           |

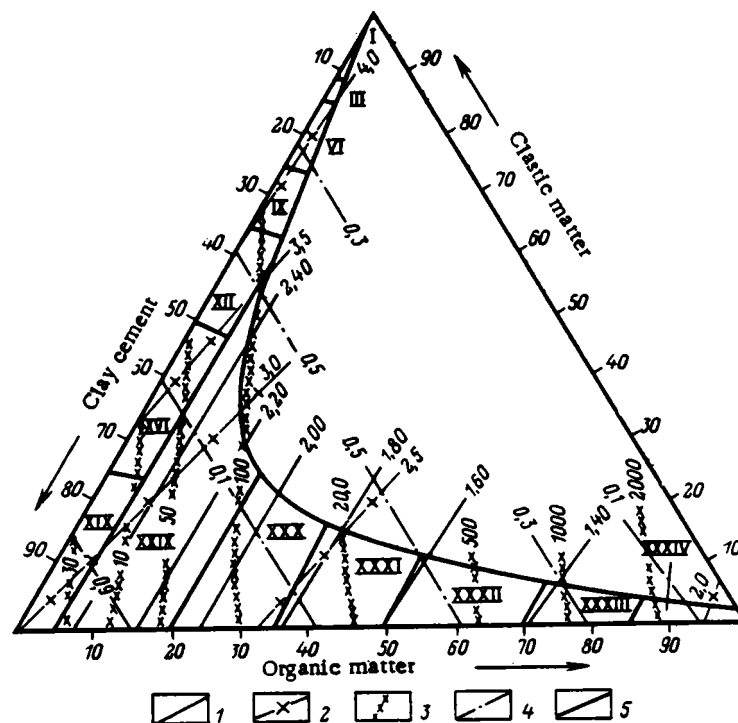


Fig. 5. Example of a chart for determination, from bore holes, coal and coal-bearing rocks, petrotypes and their composition (Usa deposit, Pechora Basin, coal metamorphism stage VIII (F); lithologic-geophysical step I). 1) Density of waterlogged rock, g/cm<sup>3</sup>; 2) velocity of elastic P waves km/sec; 3) electric resistivity,  $\Omega$ m; 4) natural gamma radiation intensity, rel. units; 5) boundaries of petrotypes. For petrotype names see Table 3.

The analysis of geologic-geophysical information for the various basins has established that the same petrophysical types at the same stage and step of epigenesis are characterized by the same indicators. By generalizing this information, a maximum list of petrophysical types of coal-bearing rocks, coals, and coaly rocks can be compiled, which can be identified by geophysical investigations in the profiles of bore holes in various coal deposits and coal basins. The list is comprised of 34 petrotypes, including 28 describing rocks and 6 describing coals and coaly rocks [5]. These petrotypes differ substantially in their degrees of alteration. A typical petrophysical profile of a geosynclinal coal basin encompasses a coal-bearing bed, with the varieties of coals ranging from peat bogs to anthracite; measuring 12,000 m in thickness (20 stages of metamorphism), and including the set of rock varieties from clay sediment to clay schists of the same thickness (20 stages of epigenesis). Four phases of rock alteration have been defined on this basis: syngensis, diagenesis, epigenesis, and metagenesis. The totality of rocks and coals traced through these phases (a total of 136 petrotypes) has been called a generalized classification of coal-bearing rocks and coals (Table 1). The full names of petrophysical types identified are formulated according to the commonly used method suggested by Shvetsov [6], taking into account granulometric and optimal material composition of rocks and coals.

A new generalized classification has thus been created which encompasses and describes comprehensively coal-bearing rocks, coals, and coaly rocks. In contrast to previous classifications, it rests on a much larger number of objective characteristics of rocks and coals. Each petrophysical type is described in terms of 28 features. With this new classification the lithology of coal deposits can be studied in greater detail and more objectively; geophysical methods can be used more extensively to determine the physicomachanical properties of rocks and predict their stability in the course of mining; in addition, the petrophysical types of rocks in the profiles of coal deposits and coal basins of the USSR can be standardized.

In order to standardize notations, unified symbols for petrophysical types of rocks and coals are suggested (Fig. 1); their introduction constitutes the first step toward a generalized classification of rocks.

In practice, one has to proceed to the second stage of classification for taking into account the specific features of rock lithology in each deposit and even segment. This requires compiling a specific lithologic-geophysical classification taking account of the particular features of the reconnaissance objects by selecting from the generalized classification those petrophysical types observed in the reconnaissance segment. Petrotypes not included in the generalized classification may occur in some segments. The classification, for example, does not cover low- and medium-coaly siltstones, which have only a local occurrence amid the coal-bearing rocks of Kuznetsk Basin.

As an illustration, we will give the lithologic-geophysical classification of coal-bearing rocks and coals of the Usa deposit in the Pechora Basin. From studies in parametric bore holes in the profile of this deposit, of a total thickness of 1200 m, which contains bituminous coals of metamorphism stages VII (G) and VIII (F), we identified five lithologic-geophysical steps, including 23 petrophysical types of enclosing rocks with specific petrographic characteristics (Table 2), the petrographic characteristics of six petrotypes of coals and coaly rocks (Table 3), the composition and petrophysical characteristics of enclosing rocks satisfying the separation criterion (Fig. 2), and the geochemical characteristics of rocks (Fig. 3). On the basis of these data, we have also constructed a chart for determination of the composition (percentage content of clastic material and clay and carbonate cement) and granulometry of enclosing rocks based on geophysical measurements in bore holes (Fig. 4).

The chart is constructed by plotting points in the coordinates of a triangle with certain values of composition of seams (along the sides of the triangle) and their physical parameters (isolines inside the triangle). With these data (the contents of carbonate cement and granulometry of clastics), the boundaries of petrophysical types of rock compositions and granulometries have been drawn.

For practical use of the chart, points should be plotted on isolines or between them, representing the physical properties measured in the bore hole through the seam being studied. Isolines of the various physical properties of the seam are drawn through these points, which will cross at a point or form a small error polyhedron. The isoline cross-point or the center of error polyhedron defines in the coordinates of the triangle the number and name of the petrophysical type and its composition.

The chart helps identify the petrophysical types and their composition in the profile of the first lithologic-geophysical step in all bore holes on a segment of exploration regardless of the availability of a core from the bore hole. For other lithologic-geophysical steps in the profile of a deposit similar charts are constructed. The diagram for determination of the petrophysical types of coals and coaly rocks and their compositions is plotted similarly (Fig. 5).

Collectively, the data of Tables 2 and 3 and Figs. 2 and 3 for a coal deposit or a reconnaissance district constitute the lithologic-geophysical classification of rocks and coals of the deposit or the district.

In the profile of the Usa deposit, 23 petrophysical types of rocks and six petrotypes of coals and coaly rocks were thus identified (a total of 29 petrotypes). The composition of rocks varies slowly and remains practically constant within the 1200 m thick profile. The composition of coals changes more rapidly: at the top of the profile the coals belong to metamorphism stage VII (G), while at the bottom they belong to stage VIII (F), i.e., are divided into two stages by composition. The physical properties of rocks and coals experience an even faster variation; the profile was thus divided into five lithologic-geophysical steps. Within each step the physical properties of rocks and coals are assumed to be constant for all practical purposes, while in the profile of the deposit they change five times. In the petrophysical characteristics of rocks and coals used in this classification (see Fig. 2 and Table 2), they all belong to the first lithologic-geophysical step of the profile of stage VIII (F).

The classification thus performs two functions: a global function encompassing all coal deposits and basins (a generalized classification) and the specific function of describing the features of an area being explored (lithologic-geophysical classification).

The generalized classification of coal-bearing sediments (rocks and coals) and the detailed lithologic-geophysical classifications for the individual deposits and reconnaissance areas constructed on this basis make it possible to standardize on a national scale for the Soviet Union the geologic-geophysical methods of detailed documentation of coal bore holes and the definitions of the petrophysical types and their compositions. This standardization is important both for theoretical studies and for practical purposes.

The classification has been tested at Pechora, Donets, and Kuznetsk Basins. The trials confirmed the high reliability of determination of the mineral, geochemical, and granulometric composition of rocks, as well as petrophysical and epigenetic characteristics of these units based on geophysical bore hole explorations.

This classification of coal-bearing sediments can thus be of great help in improving the reliability of scientific descriptions of the geology of coal deposits and improving the quality of their exploration. A speedy introduction of this classification into coal geology is desirable.

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#### ANCIENT PHOSPHORITES OF MONGOLIA

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UDC 553.64(517)

The formation settings of Mongolia's phosphorites are studied. By using the method of formation analysis it is shown that large deposits of phosphorites of the Vendian-Early Cambrian time were formed by biogenic diagenesis in arid shelf basins.

Ancient phosphorites of Mongolia are associated with terrigenous carbonate units of Vendian-Cambrian phosphate accumulation epoch, which left traces on almost all of the world's continents. Phosphorite deposits and signs in Mongolia form the large Khubsugul Basin in the north of the country (Fig. 1). Potential phosphorite-bearing complexes exist in the western and southern parts of the country; complexes with potential phosphorite presence are widespread in which small signs of minerals have been identified in the last few years.

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Ministry of Geology and Mining of the Mongolian People's Republic, Ulan-Bator. Translated from *Litologiya i Poleznye Iskopaemye*, No. 1, pp. 94-104, January-February, 1987. Original article submitted April 25, 1985.



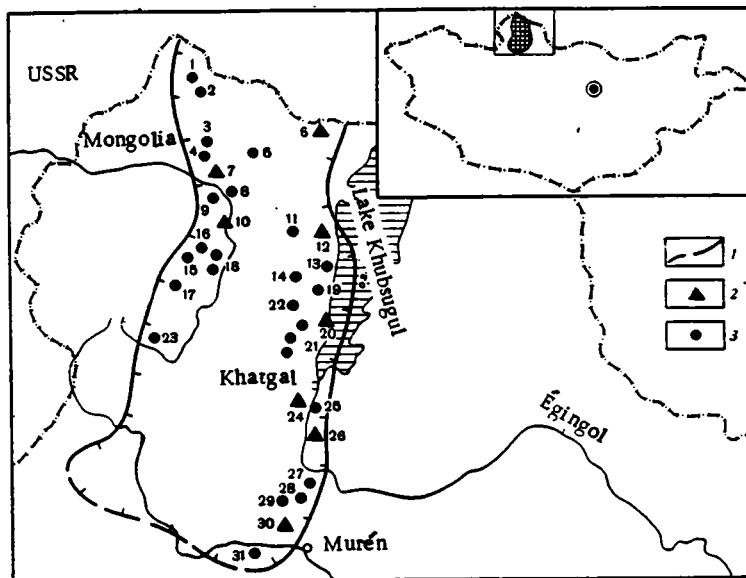


Fig. 1. Schematic map of phosphorite deposit and phosphate occurrence signs, Khubsugul Basin. 1) Basin boundaries; 2-3) deposits and phosphate signs. 1) Dértrug, 2) Targalulin, 3) Middle Tengisin, 4) Utszégín, 5) Ust'khabkhai, 6) Ukhagol, 7) Khogorga, 8) Eastern Dodnur, 9) Kharma, 10) Tsaganur, 11) Maratuinul, 12) Uleindaban, 13) Chzhiglig, 14) Kharagol, 15) Khugéingol, 16) Bayangol, 17) Témensulta, 18) Darkhat group, 19) Kharasugul, 20) Khubsugul, 21) Arasan group, 22) Bagat-sagaangol, 23) Khunkh, 24) Bérkhimula, 25) Khurennur, 26) Mankhanula, 27) Ikhtsakhir, 28) Sultologol, 29) Dorozhnoe, 30) Burénkhan, 31) Tsaganuruus.

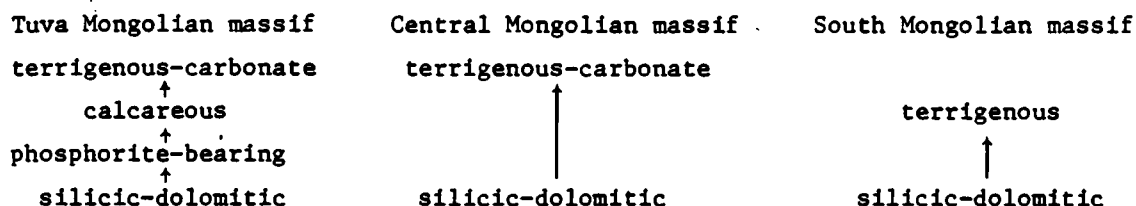
#### GEOLOGY OF PHOSPHORITE UNITS

The continental slopes in which phosphorite-bearing entities accumulated were the sialic basements formed by the beginning of the Early Riphean; this hypothesis is supported by the set of formations of the constituent complexes. There are three large massifs — Tuva-Mongolian, Central Mongolian, and South Mongolian — identified in Mongolia's territory in which Vendian–Early Cambrian terrigenous carbonate units are common (Fig. 2). They cover as a nearly continuous canopy the southwestern and central Tuva-Mongolian massif (the Khubsugul series), form a wide strip in the western and southern slopes of the Central Mongolian massif (Tsaganolom, Bayan-Gol, Salany-Gol, Ortsog suites, and others), and can be traced by isolated outcrops of dolomite limestone and other rocks (Barginoba suite and its analogs) within the South Mongolian massif. The lower boundary of these units is defined by the structural disconformities and local breaks in sedimentation, while the upper boundary is defined nominally by disconformal interface with the overlying Upper Cambrian–Ordovician coarse-clastic complexes.

The age of terrigenous carbonate formations, based on organic remains, is defined as Vendian–Lower Cambrian, with local Middle Cambrian rocks (in the southern Khubsugul region). In the South Mongolian massif the upper age boundary probably covers only the lowest strata of the Lower Cambrian or does not go beyond the Vendian. These strata are approximately 6000 m thick.

The composition of terrigenous carbonate formations has been studied in detail for the Khubsugul region and in the Dzabkhan River basin and less extensively in other parts of the country. The following vertical formation series are identified in these massifs: (see top of next page).

We will describe some of the features of the formation series of Tuva Mongolian massif [8, 11, 12, 14], which encompasses the Khubsugul phosphorite-bearing basin (Fig. 3). The bottom silicic-dolomitic formation begins with basal layers composed of small pebble conglomerates with carbonate cement and consists mainly of gray and creamy, massive, locally



breccialike dolomites with small Vendian oncolitic bioherms. In the southern Khubsugul region thin (up to 2 m) dark- and light-gray silicic rocks appear amid dolomites, exhibiting imprints reminiscent of Vendian skeletonless fauna.

At 300-500 m above the foot of the Khesen suite within this formation, "floating" medium-rounded carbonate pebbles occur amid dolomites in the southern Khubsugul region, which apparently made up some of the poorly consolidated dolomitic sediment. "Floating" tillitelike conglomerates have also been described at this level near the western shore of Lake Khubsugul. Their pebbles consist of well-rounded silicic rocks, less frequently dolomite. Dolomite is overlain by finely stratified clay-silicic clay-carbonate schist, massive phthanite, beds of rich phosphorites, and less often bituminous limestone. No skeletal forms except for benthic brachiopods, chiolites, and chiolithelminths have been found in these phosphorite-bearing units.

The phosphorite-bearing silicic dolomitic formations exhibit a complex composition both in vertical and lateral directions. At the north of the Khubsugul trough it is crowned by a light-gray massive dolomite bed approximately 100-300 m thick. In the south of the trough, at the bottom of the above-phosphate member, stratified limestone prevails among carbonate rocks; the limestone thickness is not less than 400 m; at the top of the series gray and dark-gray dolomites are predominant (1500 m).

Rare limestone layers occur amid dolomites. The dolomites have a mosaic structure. The space between dolomite grains is filled with calcite. Stromatolite structures have been described amid dolomites in the south of the Khubsugul trough. Silicic concretions of various shapes and sizes are frequently found in this formation. The number of phosphorite beds varies from 1 to 5; they range in thickness from 5 to 100 m. Along the eastern side of Khubsugul trough they stretch for 30-40 km; in other locations their average length ranges from 1-3 km. Within the western side of Khubsugul Basin the number of phosphorite beds is increased, while their thickness is diminished; finely stratified silicic rocks and dolomites are predominant in the formation in that area, while the contribution of terrigenous material declines compared with the eastern and southern sides.

The silicate dolomitic formation is crowned by a horizon of clastic rocks whose pebbles consist of quartz chalcedony, microquartzite, phosphorites, and less dolomite and limestone. The matrix consists of clay and silicic material. So-called sandstone phosphorites with a low phosphorous anhydride content are confined also to this horizon.

Generally, within the phosphorite-bearing silicic-dolomitic formation, as one moves away from the eastern side of Khubsugul trough westward, dolomites and coarse-clastic facies disappear from the profile after the first few kilometers and gradually are replaced by uniform, finely stratified, dark-gray, locally black limestones and clayey schists with frequent thin silicic rock layers. Further on in the Dzhida and other zones, they give way to the facies of contemporaneous substantially volcanogenic complexes.

The next calcareous formation corresponds approximately to the Khoridula (Érkhélnur) suite and consists mainly of dark-gray organogenic and chemogenic limestones with less frequent interlayers of dark-gray silicic rocks and phthanites (2500 m).

Organogenic limestone is formed of large bioherm reefs containing abundant archeocyathic structures. The archeocyathic reefs are widespread in the southern Khubsugul region and can be traced northward meridionally along the central part of Khubsugul trough, almost to the border with the Soviet Union. Isolated reefs have been noted in contiguous contemporaneous structures formed of sedimentary volcanogenic units. Similar archeocyathic structures are known in the neighboring Sangilen and Bokson-Sarkhoi troughs.

Frequent patterned structures are characteristic of the calcareous formation. These structures were apparently formed when semicompact sediments were exposed during the course of diagenesis to bottom currents in which bottom or burrowing organisms could be active.

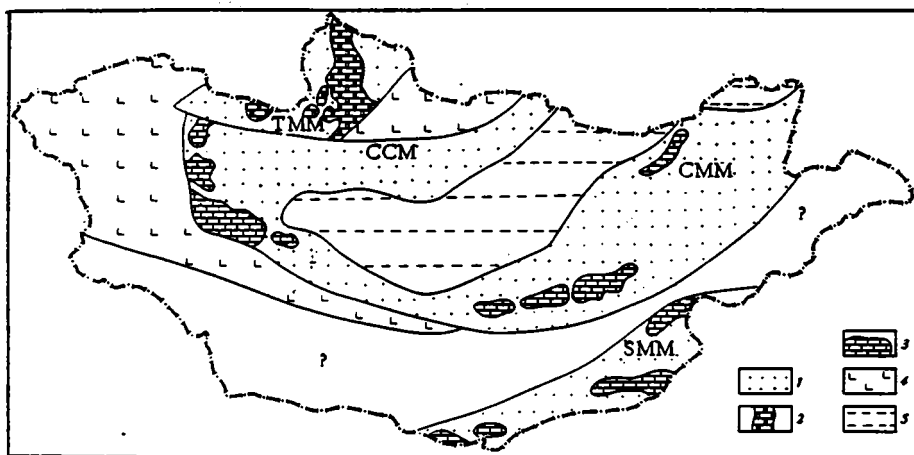


Fig. 2. Occurrence of Late Riphean–Early Cambrian terrigenous carbonate units. 1) Ancient stable massifs; 2) outcrops of terrigenous carbonate phosphorite-bearing formations; 3) outcrops of potentially phosphorite-bearing terrigenous carbonate formations; 4) areas with predominant volcanogenic sediment accumulation; 5) areas with predominant terrigenous accumulation. TMM) Tuva–Mongolian massif; CMM) Central Mongolian massif; SMM) South Mongolian massif.

Traces of turbidite currents are well pronounced amid stratified limestones at some sites. Trilobites and brachiopods of a benthic habitat have been described in this limestone.

The calcareous formation in Khubsugul trough gradually, up the profile, gives way to greenish and green-gray sandstone, siltstone, and gritstone, which in turn are replaced by dark-gray limestone interstratified with thin silicic rocks (Ukhutologoi and Udzhigingol suites).

In the southern part of Khubsugul trough and further in the western and northern margins of the Dzabkhan zone, the sediments of the terrigenous-carbonate formation are partly or completely replaced in the lateral direction by diabase or andesite porphyrites and their tuffs. This formation is characterized near southern Khubsugul region by Lower and Middle Cambrian trilobites. This suggests that phosphorite-bearing formations of the Tuva–Mongolian massif consist largely of terrigenous-carbonate rocks. Volcanogenic units are absent or scarce, occurring on limited areas at the top of the profile.

The potential phosphorite-bearing units described within the Central Mongolian and South Mongolian massifs also consist (up the section) of silicic-dolomitic, terrigenous-carbonate, and terrigenous formations [1]. These formations are similar in structure, with phosphorite-bearing silicic-dolomitic formation of the Tuva–Mongolian massif displaying dark and dark-gray dolomite-silicic rocks, limestone, sandstone, siltstone, and gritstone. Within the Tsaganolom and Ortsog suites [1] a low (1–10.7%)  $P_2O_5$  content, locally rising to 25.5%, has been determined. The heightened  $P_2O_5$  content in the rocks of silicic-dolomitic and terrigenous-carbonate formations is indicative of prospects of phosphorite-bearing deposits in these areas. In similar units of the Late Riphean–Early Paleozoic of the northern margin of the Chinese (North China) Platform, phosphorite ores have been described [7].

#### STRUCTURE OF PHOSPHORITE-BEARING MEMBERS

The phosphorite-bearing members of each deposit and ore show in the Khubsugul Basin have common traits as well as specific features [8, 10, 12]. In almost all deposits the horizon underlying the bottom phosphorite bed consists of breccialike dolomites, carbonate conglomerates, and black tabellar limestone. The bottom phosphorite layer usually is the most productive in each deposit. In Burenkhan deposit it has a mean thickness of 60 m, while in other deposits it is split into three to five seams of a few tens of meters thick each, separated by phosphatized or phosphorus-free silicic limestone, flint, and dolomite. The phosphorite seam is overlain by a horizon of black flint up to 4 m thick (Fig. 4).

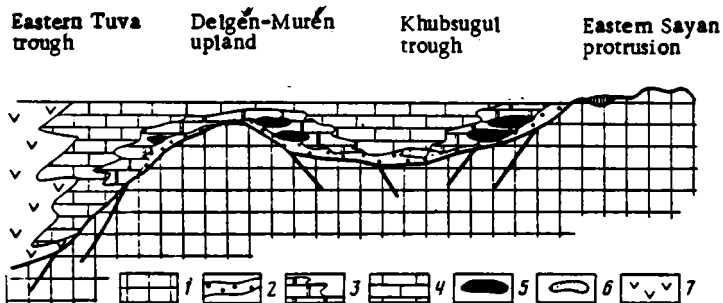


Fig. 3. Schematic chart of accumulation of phosphorite-bearing Khubsugul series in North Mongolia. 1) Bed of formations; 2) basal layers; 3) dolomites; 4) limestones; 5) phosphorites; 6) bauxites; 7) volcanites.

The bottom bed is most consistent along the course, while the other beds wedge out or give way to slightly phosphorized dolomite or silicic rocks. The beds decrease in thickness at a distance from the side of the basin and gradually wedge out. At the Khubsugul deposit phosphorite beds of the bottom layer are overlain by a dolomite stratum with limestone horizons about 100 m thick. In the Burenkhan deposit this horizon consists mainly of limestone about 1500 m thick with less frequent discontinuous flint and phosphorite horizons.

The following approximate succession of sedimentation rhythms can be conjectured: silicic and terrigenous rocks — phosphorites — silicic rocks — dolomites (limestones). The development of the phosphorite-bearing formation is completed by the deposition of low-quality phosphorite-bearing beds of the second layer. The beds consist of sandstone, gritstone, conglomerate, schist, and dolomite, with phosphate material present as grains, clots, thin layers, and fragments, along with other clastic matter. The matrix consists of dolomite and clay rocks. The phosphorite-bearing member is covered conformably by a thin dolomite layer, succeeded by a thick bed of organogenic limestones.

The foregoing picture shows an extremely complex structure of the phosphorite-bearing members in the Khubsugul Basin. The principal beds are traced with interruptions along the western and eastern sides, displaying two fairly distinct phosphate accumulation levels (see Fig. 3).

#### PHOSPHORITE COMPOSITION

Macroscopically, Khubsugul phosphorites are black rocks, resembling flint or bituminous limestone of a massive (aphanitic), stratified, or granular (pelletlike) structure. Il'in and Ratnikov [12, 13] have studied the phosphorite ores of this basin. They have identified aphanitic (monophosphate), layered, microgranular (pellet), brecciated, and clastic petrographic phosphorite varieties. These are typical for the main bottom layer of phosphate development. The petrographic phosphorite varieties form no distinct distribution patterns. They occur in almost all deposits in various proportions. Massive amorphous varieties with a minor quantity (3-4%) of insoluble residue are classified as monophosphates. Both the grains and the matrix are formed of a phosphate material in the monophosphates. Slightly visible rounded textures with a quartz grain at the center are sometimes seen amid monophosphates. Monophosphates with alternating light and dark thin strips are frequent. Stratified phosphorites of alternating monophosphate and dolomite strips are widespread. The bottom contacts of phosphate strips are sharp, while the upper contacts are blurred, as though the phosphate strips gradually become dolomite strips. The dolomite strips sometimes contain phosphate fragments or grains. Pellet phosphates include granular, lacustrine, and oolitic varieties consisting of micrograins (0.05-0.2 mm) of a concentric structure or of rounded amorphous phosphate. Inside the pellets quartz or feldspar grains are frequent. The cement is of the carbonate or silicic-carbonate composition; sometimes the pellets are closely packed. Brecciated phosphorites are quite common. They were formed by intrastratal breakage of stratified phosphorite layers.

Electron microscopic investigation has shown the phosphate mass of monophosphates and stratified phosphorites to be largely amorphous, consisting of apatite crystals of 0.5-1.0  $\mu\text{m}$ . The crystals are either arranged at random or with a radial-fibrous orientation.

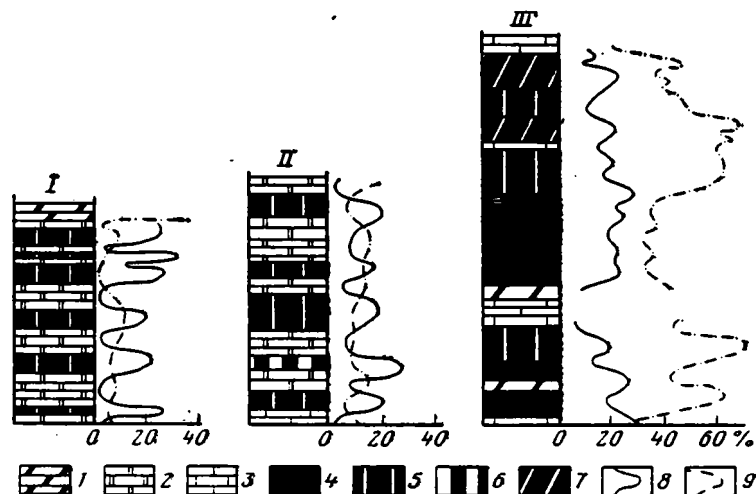


Fig. 4. Phosphorite-bearing members, Khubsugul Basin. 1) Flint; 2) dolomite; 3) limestone; 4) nonlayered monophosphate; 5) layered carbonate phosphorite; 6) layered silicic-carbonate-phosphorite; 7) layered silicic phosphorite; 8)  $P_2O_5$  content, %; 9) precipitate content, %. I-III) Deposits (I - Tsaganur; II - Khubsugul; III - Burénkhan).

Granular phosphorites form bunchlike or radial-fibrous aggregates of a subcollomorphous texture. Based on the microtextural features of the phosphate matter, structureless (monophosphate, stratified, and breccia phosphorites) and pellet-type (granular, microgranular, oolitic, etc.) varieties can be distinguished. The phosphate matter in phosphoritic ore consists of crystalline or subcolloid aggregates formed of the isomorphous series: fluorapatite-fluorhydroxylapatite.

Phosphorite ores consist of phosphate, carbonate, and silicic rocks. Depending on the proportions with carbonate and silicic rocks, the type of ore and its quality is defined. The carbonate and silicic-carbonate phosphorites are predominant in the deposits of the eastern and southern sides of the Khubsugul Basin, while silicic varieties are prevalent on the western side. In aphanitic and stratified phosphorites,  $P_2O_5$  content varies on average from 20 to 40%, in pellet varieties from 5 to 26%.  $SiO_2$  is inversely proportional to  $P_2O_5$  content. Silicic minerals consist mainly of chalcedony and quartz.

Of the accessory elements the phosphorite ores contain lead, molybdenum, vanadium, nickel, tin, chromium, cobalt, copper, silver, strontium, arsenic, manganese, zinc, and uranium. The rocks of the phosphorite-bearing member also have a high  $C_{org}$  content (0.5-5.0%).

#### PALEOGEOGRAPHIC CONDITIONS OF PHOSPHATE ACCUMULATION

The development of phosphorite deposits is known to be affected by paleogeographic factors [2, 4, 5, 16, 17]. Paleogeographic interpretations can be derived from the above data (Fig. 5).

The variability of the formations of the silicic-dolomitic and calcareous formations and the development of biogenic reefs (from Vendian through the Lower Cambrian) shows that the surface of the continental shelf of the Tuva-Mongolian and Central-Mongolian massifs, which probably consisted of uplifted and lowered blocks, was prepared by earlier Upper Riphean tectonic processes. The coastal part of the shelf basin was probably situated approximately at the meridian of Lake Khubsugul, evidenced by the increase of terrigenous matter in that direction. In addition, the phosphorite-bearing silicic-dolomite formation tends toward the sides of Khubsugul trough as a strip of a few tens of kilometers wide. In this context, studies by Il'in [12] are of interest; he has demonstrated that the content of the dolomitic component (magnesium) in carbonate rocks of the basin increases toward the coastal zone. This suggests that dolomite precipitation in these conditions was favored by the intense warming of the coastal shelf waters.

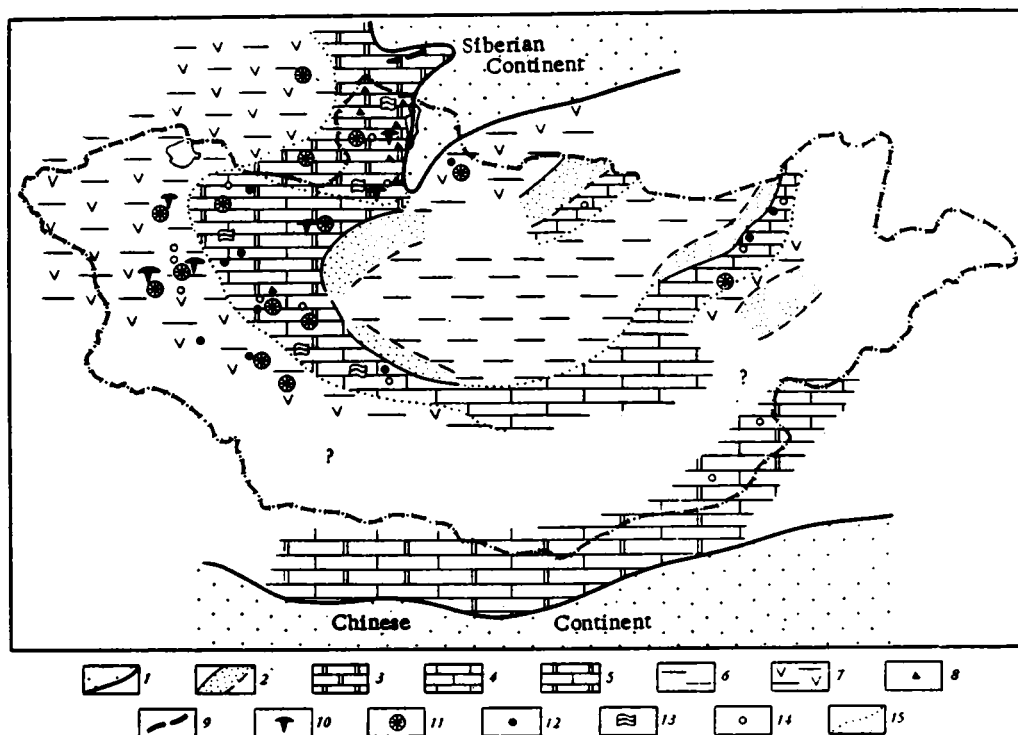


Fig. 5. Paleogeographic schematic map of the Late Riphean–Early Cambrian in Mongolia. 1) Continents and their boundaries; 2) islands and their boundaries; 3-5) shelf zones and submarine rises with predominant terrigenous carbonate sedimentation (3 – mainly dolomite; 4 – mainly limestone; 5 – interstratified dolomite and limestone); 6) internal marine basins with predominantly terrigenous sedimentation; 7) oceanic basins with predominant sedimentary-volcanogenic sedimentation; 8) phosphorites; 9) bauxites; 10-14) finds of organic remains (10 – trilobites; 11 – archeocyathids; 12 – oncolites; 13 – stromatolites; 14 – microfossils); 15) facies boundary.

We will now consider the surface topography of the shelf in the western Khubsugul region. According to [12], a gulflike paleobasin between Uriol (in the east) and Délgermuren (in the west) protrusions was situated in this area. Recent studies [14] have shown, however, that at least during the phosphate accumulation time the Délgermuren protrusion functioned as a syndimentary upland. This is confirmed by the fact that it is formed of Riphean terrigenous-carbonate rocks. In addition, the composition of the Vendian–Lower Cambrian silicic-dolomitic formation acquires a more marine character as compared with the synchronous formation in the eastern side of the Khubsugul trough. The central and western parts of the Tuva-Mongolian massif thus was a shelf zone a few hundred kilometers wide with a complex seafloor topography; the seafloor level was above the level of carbonate compensation and thus controlled sedimentation, including phosphate accumulation. The sea coast stretched submeridionally, approximately from the southern Khubsugul region in the south to the Sayan Mountains in the north. The present Délgermuren upland was probably the site of a syndimentary submarine rise, while the area of the eastern and southeastern Khubsugul region was an ancient peneplanation plane which was the source of local clastic material. On the basis of lithologic indicators, we will attempt to reconstruct the Vendian–Early Cambrian climate. Carbonate rocks forming the phosphorite-bearing and above-phosphorite formations consist exclusively of marine dolomite and limestone. Limestone, in smaller layers, is observed at the bottom of the profiles amid dolomite beds of the Khésén suite and its analogs. They occupy a predominant position in the middle and upper portions of the Khubsugul series. It has been established [18] that limestones are confined to lower latitudes, i.e., to arid and tropical climate. Reefogenic limestone of the middle portion of the Kubsugul series also indicate an arid subtropical climate of the time.

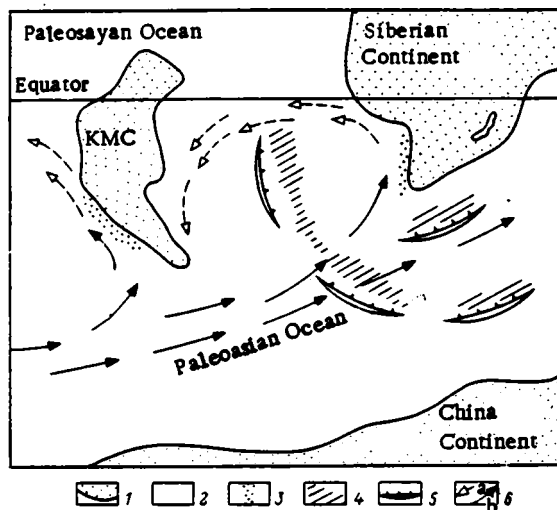


Fig. 6. Reconstruction of Vendian-Cambrian oceanic basins and position of continents in Central Asia. 1) Continents; 2) oceans; 3) phosphorites; 4) island arc areas; 5) hypothetical subduction axes and the direction of their dip; 6) sea current (a - warm; b - cold). KMC) Kazakhstan microcontinent.

Phosphorites are also indicators of a warm and slightly dry climate [16]; microgranular, granular, and oolitic phosphorites with a high  $P_2O_5$  content are formed in arid regions. The sharp drop in clay rock content in the phosphorite series profile in northern Mongolia was also apparently a sign of an arid climate. The abundance of phthanites and silicic rocks, often in association with phosphorite and dolomite, indicates their authigenic origin. At about the same stratigraphic level, bauxites are widespread at the bottom of the Bokson series of eastern Sayan, while in the Khubsugul region bauxitelike rocks (allite) are found which are also sensitive indicators of a tropical humid climate. Large accumulations of halogenic units (Usol suite and its analogs) are known at the same level in the south-eastern Siberian platform, also indicative of an arid climate.

Incomplete as it is, the description of the lithologic indicators of the Vendian-Lower Cambrian climate of northern Mongolia points to arid conditions typical for low latitudes. These data match well with paleomagnetic measurements [9].

The lithologic composition of the phosphorite-bearing formations is quite uniform (silicic-carbonate); there are no terrigenous formations of a significant thickness. This suggests that the land bordering the shelf zone on the north and east was poorly drained.

Pelitelike rocks and "floating" conglomerates, described at the base of the phosphorite-bearing formation, were probably produced by cryogenic processes in the neighboring area. The climatic indicators of the Vendian-Early Cambrian time in the territory of northern Mongolia and the reconstructed topography of the southern Siberian continent, as well as paleomagnetic data, suggest that the southern part of the continent obstructed southwestern trade winds generated by a high pressure zone. The steady southwestern trade winds gave rise to cold sea currents flowing in the same direction. The southwestern shelf of the Siberian mainland, which was situated in the arid zone, was thus exposed to a cold sea current conducive to upwelling - the rise of cold water to the surface from the depth [15]. These currents could bring biomass into the shelf zone (Fig. 6). There are grounds to assume that the shelf zones of the Tuva-Mongolian and Central Mongolian massifs opened westward and woutheastward toward Lake Dzhida zone, where contemporaneous Vendian-Early Cambrian sedimentary volcanogenic complexes developed [8, 14].

The composition of the seawater in the Vendian-Early Cambrian basin also played an important part in phosphorite formation; it can be estimated indirectly from investigations of the composition of the sediments of the time [5, 17-19]. Widespread dolomites and evaporites, silicic rocks, and phthanites and the regional contamination of terrigenous-carbonate units with organic matter and phosphate suggest that the water of the Vendian-Early Cambrian paleocean was enriched in magnesium, chlorides, silica, and organic matter. The bottom of the Khubsugul series is particularly rich in organic carbon ( $C_{org} = 0.1-2.0\%$ ). The data of Osokin and other geologists on Burénkhan deposit show that  $C_{org}$  in phosphorites of the southern part of the basin had an even higher content (0.5-5%), coinciding with the thriving of nonskeletal and skeletal organic forms in the oceans during the Vendian-Cambrian. In addition, Borshchevskii et al. [6], studying the isotopic composition of oxygen from Khubsugul phosphorites, have concluded that phosphorites were formed biochemically in marine epicontinental basins, which had an uninterrupted hydrodynamic communication with the ocean

and a high biological productivity. Assuming that the primary main source of phosphate matter in the world ocean was continental erosion [7], the authors concluded that biogenic factors were the main carriers of phosphate in the development of large phosphorite deposits. The subsequent transformation of phosphate matter in phosphorites probably took place during the diagenetic stage of sediment lithification [3, 4].

\* \* \*

The Khubsugul phosphorite basin in the north of Mongolia and the potential phosphorite-bearing structures of western and central Mongolia make part of an extensive Asian phosphorite-bearing Late Proterozoic-Cambrian province. The ancient phosphorites of Mongolia developed both on the epicontinental shelf of the southern tip of the Siberian platform (the Tuva-Mongolian massif) and on the slopes of intraoceanic rises (Central Mongolian massif). The beds of these epicontinental structures, in particular, of the Tuva-Mongolian shelf, were compounded by alternations of uplifted (Delgémuren and others) and lowered (Darkhat-Khubsugul) blocks and the submeridional blocks created during the preceding evolutionary stage.

Phosphorite formation was confined to the early periods in the general transgressive sedimentation cycle, probably associated with an interglacial epoch. The richest phosphorites of Mongolia are associated with a Vendian-Lower Cambrian silicic-carbonate formation. Of the three identifiable phosphate formation levels, in Mongolia, the Lower Cambrian (Tomot) is the most productive one. Aphanitic, stratified, and microgranular phosphorites are the prevalent petrographic varieties.

Against the background of the general complex structure of phosphorite-bearing members, phosphorites wedge out by facies toward the central part of the troughs; a coarse rhythmic pattern of phosphate accumulation has been established, which begins with terrigenous rocks and ends with carbonate accumulation.

Ancient phosphorites were formed at low latitudes in arid climates. Mongolia's phosphorites are probably of a biogenic diagenetic origin. Thus, during the Vendian-Early Cambrian favorable combinations of paleogeodynamic and paleogeographic settings existed in the area of the Tuva-Mongolian and Central Mongolian massifs for the formation of considerable phosphorite deposits.

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# CLAY MINERALS OF THE LOWER AND MIDDLE JURASSIC DEPOSITS OF WESTERN DAGESTAN

Yu. O. Gavrilov and S. I. Tsipurskii

UDC 552.52:551.762(470.67)

In the article, we investigate the distribution of clay minerals in a 9 km thickness of Lower and Middle Jurassic terrigenous sediments. It is shown that from top to bottom along the section and also in the direction of increasing dislocation of strata, from a zone of monoclinial bedding to a zone of intense crumpling, a change of clay-mineral association from hydromicaceous-kaolinitic-chloritic to sericitic-chloritic takes place. A change in the polytypic modifications of micaceous minerals from 1M to 2M also takes place. The diverse transformations of clay minerals which are found here are connected with intense catagenetic and metagenetic processes and also with the effect upon the rock of lateral stress caused by the appearance of cleavage.

Lower and Middle Jurassic sandy-clayey sediments are distributed over a wide area of the Northeastern Caucasus. The deposits occurring within the different tectonic structural zones here have undergone postdiagenetic transformations to various degrees. The goal of our present investigation was to clarify the mineral composition of the clay minerals and character of their alterations from the most ancient Middle Liassic deposits in the region, which were subjected to the maximum action of catagenetic and metagenetic processes (cleaved slates), to the comparatively weakly altered argillites of the Middle Jurassic.

The section of Lower and Middle Jurassic sediments found in the Aivar Koisu river valley (the mouth of the Sulak River) is suitable for investigating this problem (Fig. 1). The river cuts through the Bokovoi Range anticlinorium, where Middle Liassic sediments, replaced by younger sediments to the north (right up to the Bathonian substage), are exposed. The sources of the Aivar Koisu, Dzhurmut, and Khzanor rivers drain toward a depression located to the south of Bokovoi Range and infilled with Upper Toarcian sediments of the Bezhitin suite.

Structure of the Lower- and Middle-Jurassic Strata. The Lower and Middle Jurassic section along the Aivar Koisu River (Fig. 2) consists of strata (sandy-clayey sediments) with a total thickness reaching 9000 m. The stratigraphy of the Jurassic sediments was worked out by various investigators [1, 15, 17, 18, and others] and refined in recent years by the reports of A. I. Gushchin and D. I. Panov [4].

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Institute of Geology, Academy of Sciences of the USSR, Moscow. Translated from *Litologiya i Poleznye Iskopaemye*, No. 1, pp. 105-121, January-February, 1987. Original article submitted February 28, 1986.

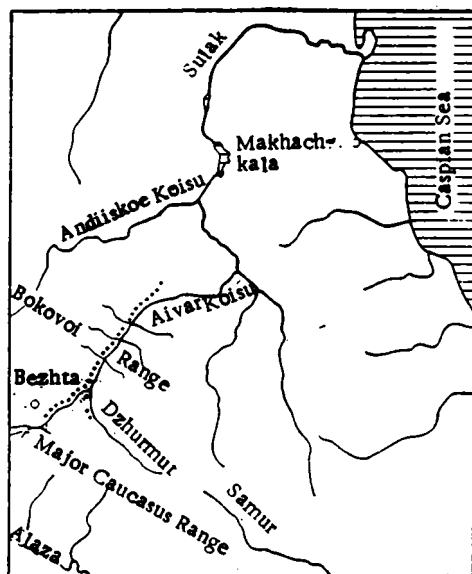


Fig. 1. Distribution map of sections of Lower and Middle Jurassic deposits exposed in the Aivar Koisu river valley (locations of the section is indicated by dots).

Sediments of the *Middle Liassic* (Upper Pliensbachian) occur at the base of the  $J_{1-2}$  section (the floor of which is not exposed). They are broken up into blocks by large-scale faults; hence, it is difficult to piece together a continuous section. When the faunal characterization is poor, it is possible to differentiate the deposits into a series of strata according to lithological criteria [4]. The following packets can be differentiated among the Lower and Middle Jurassic deposits: 1) fairly clean clay slates; 2) banded slates which are represented by a rhythmic alternation of dark, almost black, clayey and grey, silty laminae with thicknesses of several centimeters; 3) a flyschoid alternation of clay slates and fine-grained sandstones (interbeds with thicknesses of 0.05-0.2 m). Sandstone packets with beds reaching several meters in thickness are comparatively few, and packets with beds reaching several tens of meters are rarer. In characterizing the series as a whole, one should note that clayey and aleuritic rocks predominate; the portion of sandstones is significantly smaller. The sandstones are principally represented by fine-grained varieties, primarily of a quartz composition (80-90%). Feldspars and mica constitute 10-15%; the content of other minerals, including accessory minerals and rock fragments, is small (a few percent). The thickness of the Middle Liassic series in the Aivar Koisu River region is 3000-3200 m.

The contact of the Upper Pliensbachian deposits with the Toarcian deposits is tectonic. The *Toara* section reaches 3500 m. It is also composed of sandy-clayey deposits; but the role of sandy material is substantially increased here. Thick horizons of massive sandstones occur in the upper portion of the Lower and Middle Toarcian series (Fig. 2). In the Upper Toarcian deposits, sandy beds (5-40 m) alternate with clayey-silty packets (up to 100 m) in various combinations. In some intervals, the series takes on a flyschoid appearance. The sandstones are fine and medium-grained; cross-bedding and traces of rippling can often be found. Some clayey packets contain very large numbers of interbeds consisting of siderite concretions. Interbeds of concretionary conglomerates and also other traces of bottom currents which scoured deposited sediments can be found in the argillites.

The *Karakhs sk suite* is found at the very top of the Toarcian and the Aalenian. It consists mainly of sandstone (the thicknesses of the sandstone beds reach several tens of meters), with quantitatively subordinate clayey and siltstones deposits. The *Kharakhs sk suite* is coal-bearing over almost the entire territory of Dagestan. Interbeds of coal in the section along the Aivar Koisu River are small in number and thin (several decimeters). The sandstones are often cross- and wavy-bedded with traces of subaqueous slumping and local subaqueous scouring. Many concretions are found in the argillites and sandstones. The sandstones, as in the lower-lying deposits, are predominantly quartz (80-90%) and feldspars (10-20%). Fragments of quartzites, effusives, flinty rocks, micas, accessory minerals, etc. are found in small quantities [17]. Fine-grained varieties of sandstones predominate.

The *Igatlsk suite* (approximately 170 m) overlaps the *Kharakhs sk suite* and is represented by siltstones and fairly clean, dark, brownish-black argillites containing zonal dolomitic-sideritic concretions and some interbeds of concretionary conglomerates. Individ-

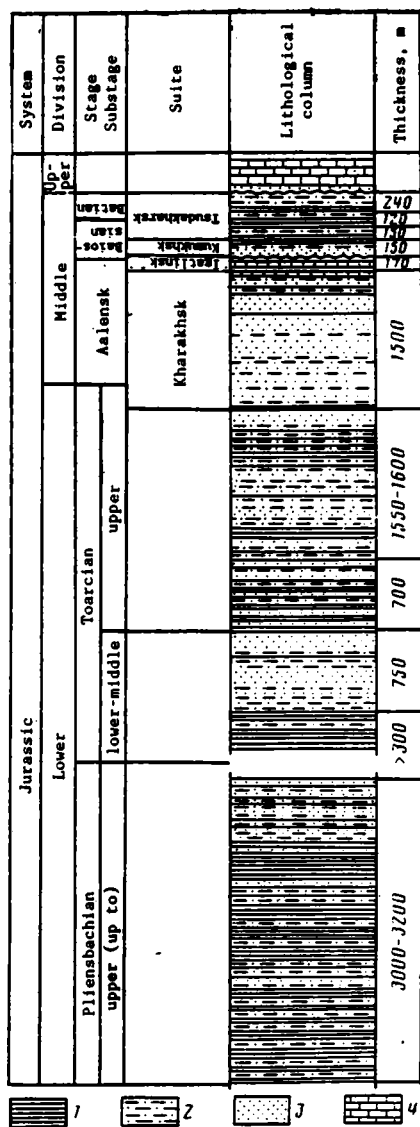


Fig. 2. Lithologic-stratigraphic column of a section of Lower and Middle Jurassic deposits along the Aivar Koisu River. 1) Argillites, slay slates; 2) siltstones; 3) sandstones; 4) limestones.

ual, thin (several decimeters) beds of limestones have been noted. The sandstones comprise a packet interstratifying with siltstones (35 m) in the center of the suite.

Deposits of the *Kharakhsk suite* lie above, with scouring on the underlying siltstones (150-160 m). In their lower portion, they consist of fine- and medium-grained greenish-gray, massive sandstones (120 m); in their upper portion, they consist of clayey-silty rock.

The *Tsudakharsk suite* (subdivided into the Khindagsk, Mogokhsk, and Karadagsk beds) is represented basically by clayey and clayey-silty deposits with individual packets (10-15 m) of interstratification within (several decimeters) sandstone layers. Some argillite intervals are enriched with a number of interbeds of siderite concretions (the Mogokhsk beds). Large (1-2 m in diameter) limestone lenses also occur. The thickness of the suite is 500-520 m.

South from the anticlinorium of the Bokovoi Range (Fig. 3), outside of the primary belt of occurrence for Toarcian deposits, deposits of the Bezhitin suite (Upper Toarcian) occur in thicknesses of approximately 1000 m. Clayey and clayey-silty deposits play the chief role here, but packets of flyschoid interbeds consisting of clayey, silty, and sandy rocks also often occur. The thicknesses of the sparsely occurring sandy beds rarely exceed 2 m.

Character of the Bedding and Dislocation of the  $J_{1-2}$  Deposits. As is evident from the profile (Fig. 3) constructed along the left bank of the Aivar Koisu River and the Dzhurmut River, the degree of dislocation of beds differs in different areas of the profile. In the

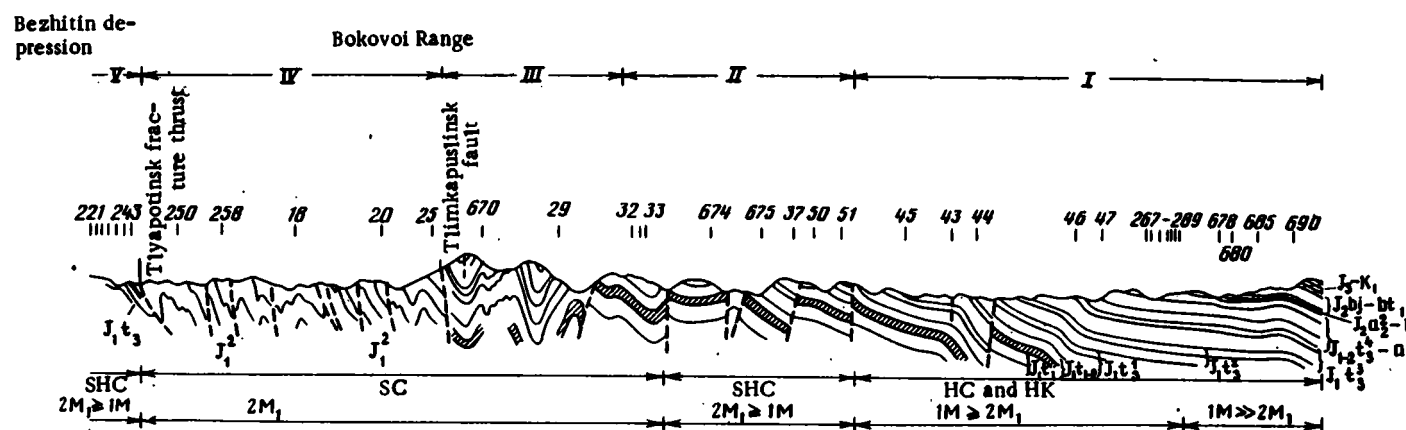


Fig. 3. Distribution of associations of clay minerals and polytypic modifications of hydromicas on a geological profile through Bokovoi Range and the Bezhitin depression (profile constructed by A. I. Gushchin along the left bank of the Aivar Koisu). I-V) Zones characterizing different degrees of bed dislocation (I - monoclinal, II - box folds and steep flexures, III - upright arched folds, IV - sharply inclined and overturned folds, V - arched folds). The associations of clay minerals are: HK) hydromicaceous-kaolinitic; SHC) sericitic-hydromicaceous-chloritic; SC) sericitic-chloritic. Horizons of uniform age are indicated by arrows.

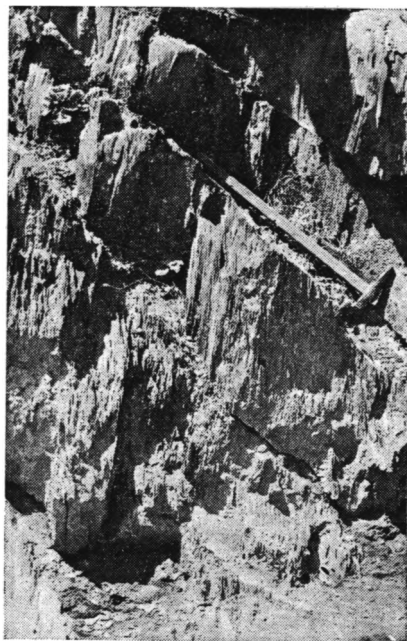


Fig. 4. Clay slates of the Middle Liassic. The plane of cleavage is situated almost vertically. The hammer lies along the sedimentational layering, which is emphasized by fine layers of sandy-silty material.

north of the profile (south of the outcrops of carbonate deposits of the Upper Jurassic), one can trace a fairly wide band of beds gently dipping toward the north (the monoclinial zone).<sup>\*</sup> The monocline is complicated by a small number of flexures and faults. The structure is made up of deposits of Upper Toarcian and Middle Jurassic Age.

The degree of dislocation of the strata increases southward with increasing proximity to the Bokovoi Range. Large-scale, steep flexures occur along with box folds complicated by faults appear. The morphology of the folds is emphasized by thick beds of sandstones (the zone of box folds and steep flexures). Simultaneously, as noted by V. N. Sholpo [19], the deeper layers in the hinges of the anticlinal folds are more strongly crumpled, but small folds with relatively sharp hinges occur near faults. A fine, deformational undulation can be traced in the layers even in areas where the layers are gently bedded. It is characteristic that a unidirectional system of fissures evidencing cleavage generation also locally occurs in the clay rocks within this zone.

Folds which are predominantly upright and arched, with relatively rounded hinges, occur further to the south. The dimensions of the folds zone of upright, arched folds are as much as hundreds or tens of meters smaller than those of the box folds. There are many ruptures of various amplitudes here, but shifts in the range of several tens of meters predominate. Cleavage is quite distinctly manifest in this zone. This character of deformation can be traced up to the Tlimkapuslinsk fault (Fig. 3) dividing the area where Toarcian deposits occur from the area of Middle Liassic deposits

The slaty strata of the Middle Liassic are markedly dislocated: folds which are crumpled into small dimensions (a few tens of meters or less) predominate and have sharp, carinate hinges. Widespread occurrence of inclined and overturned folds can be seen here. The series is broken up by numerous ruptures of different amplitudes. A recent, intense cleavage can be traced in the slates; the plane of the cleavage has a steep dip and is often almost vertical (Fig. 4). In rocks which are cleaved and crumpled into folds, "alpine" veins filled with quartz are often found. The band in which these types of dislocation occur can be divided into a zone of sharply inclined folds and a zone of overturned folds.

Southward, beyond the Tlimkapuslinsk fault (the plane of the Tlimkapuslinsk fault slopes toward the north), the sandy-clayey deposits of the Bezhitin suite (Upper Toarcian) occur. The layers here are also crumpled into folds broken by rupture faults. However, the degree of dislocation is less than that of the Middle Liassic deposits and is significantly non-

<sup>\*</sup>Zones characterizing the distinctive morphologies of the dislocations in the section along the Aivar Koisu River were initially delineated by V. N. Sholpo, though employing some different terminology [19].

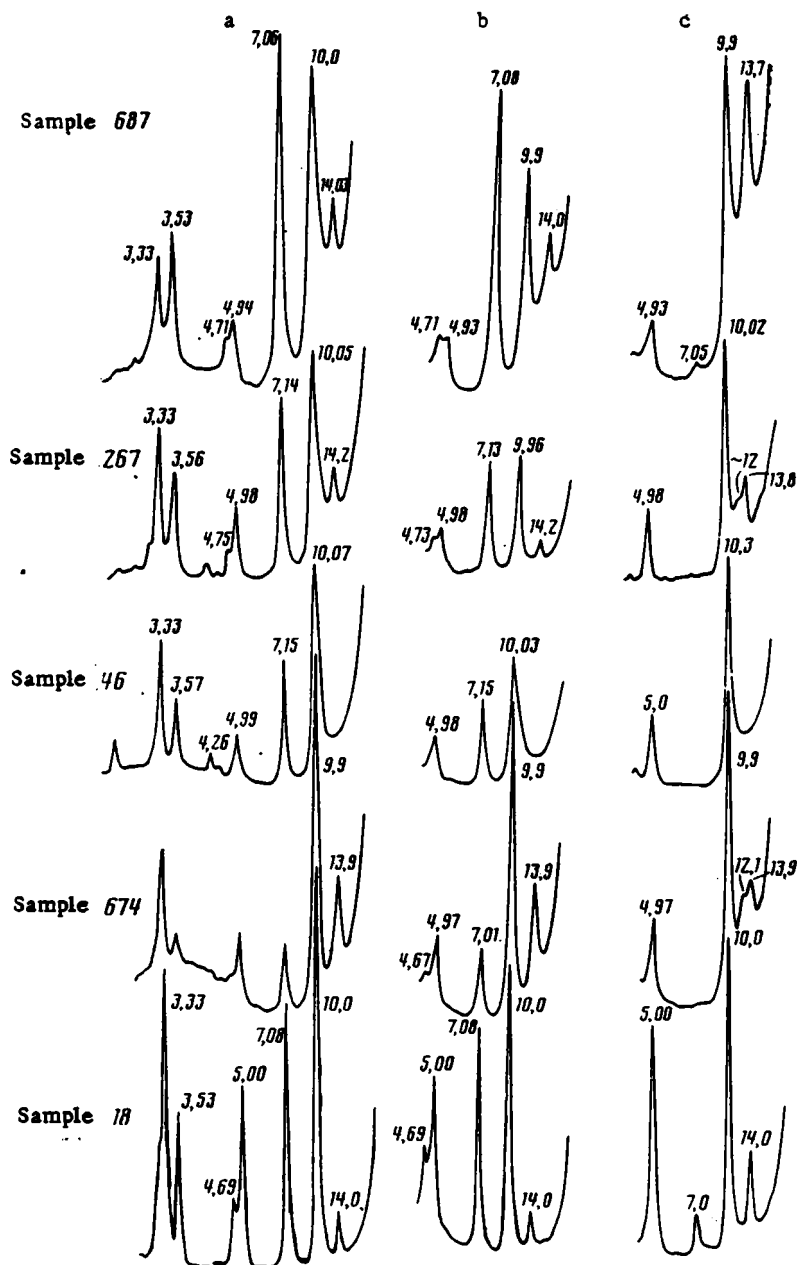


Fig. 5. Diffractograms of oriented preparations of the <0.001 mm clay fraction. Sample 18) Middle Liassic, zone of sharply inclined and overturned folds; Sample 674) Lower-Middle Toarcian, zone of box folds. Monoclinial zone: Sample 46) Kharkhsk suite, Sample 267) Igatlinsk suite; Sample 687) Tsudakharst suite. Preparations: a) natural, b) saturated with glycerin, c) heated at 550°C.

uniform within the area. In certain areas, the layers are crumpled fairly strongly and well-expressed cleavage is present; in other areas, the layers lie relatively undisturbed.

The clay deposits undergo very substantial alterations at the transition from the zone of slightly dislocated rock to the zone with intensive folding. Within the monocline, the clayey rocks are represented by argillites. Their colors vary from light- to dark-gray, but the majority of the argillites have taken on a brownish tint, the intensity of which depends upon the degree of enrichment of the rock with organic material (OM). During weathering the argillites decomposed into cloddy or flattened rock debris along the layering. Relatively well preserved sedimentational structures and textures are evident within the argillites.

TABLE 1. Polytypic Modifications and Parameters of Elementary Cells of the Micaceous Minerals

| Sample No. | Parameter of elementary cell |      |       |         | Polytypic modification of micaceous minerals and their ratios       | Suite or stage from which samples were selected |
|------------|------------------------------|------|-------|---------|---------------------------------------------------------------------|-------------------------------------------------|
|            | a                            | b    | c     | $\beta$ |                                                                     |                                                 |
| 680        | 5,19                         | 9,00 | 10,14 | 101,5   | 1M 1M $\geq$ 2M <sub>1</sub>                                        | Tsudakharak                                     |
|            | 5,19                         | 9,00 | 20,1  | 96      | 2M <sub>1</sub>                                                     |                                                 |
| 678        | 5,19                         | 9,00 | 10,15 | 101,5   | small admixture of 2M <sub>1</sub> mica and kaolinite with b = 8,94 | Kumukhsk                                        |
| 287        | 5,19                         | 9,00 | 10,18 | 101,1   | 1M 1M > 2M <sub>1</sub>                                             | Igattinsk                                       |
|            | 5,19                         | 9,00 | 20,09 | 95,7    | 2M <sub>1</sub>                                                     |                                                 |
| 46         | 5,19                         | 9,00 | 10,18 | 101,6   | Same                                                                | Karakhsk                                        |
|            | 5,19                         | 9,00 | 20,08 | 95,9    |                                                                     |                                                 |
| 44         | 5,19                         | 9,00 | 10,15 | 101,3   | 1M 1M $\approx$ 2M <sub>1</sub> ; admixture                         | Toarcian                                        |
|            | 5,19                         | 9,00 | 20,08 | 95,7    | 2M <sub>1</sub> of kaolinite with b = 89                            |                                                 |
| 51         | 5,19                         | 9,00 | 20,07 | 95,8    | 2M <sub>1</sub> 2M <sub>1</sub> > 1Md                               |                                                 |
|            | 5,18                         | 8,98 |       |         | 1Md                                                                 |                                                 |
| 37         | 5,19                         | 9,00 | 20,05 | 95,7    | 2M <sub>1</sub> 2M <sub>1</sub> > 1M                                |                                                 |
|            | 5,19                         | 9,00 | 10,15 | 101,2   | 1M                                                                  |                                                 |
| 675        | 5,19                         | 9,00 | 20,07 | 95,7    | 2M <sub>1</sub> 2M <sub>1</sub> $\approx$ 1M                        |                                                 |
|            | 5,19                         | 9,00 | 10,14 | 101,6   | 1M                                                                  |                                                 |
| 674        | 5,19                         | 9,00 | 20,09 | 95,7    | 2M <sub>1</sub> 2M <sub>1</sub> $\approx$ 1M                        |                                                 |
|            | 5,19                         | 9,00 | 10,15 | 101,5   | 1M                                                                  |                                                 |
| 33         | 5,19                         | 8,99 | 20,08 | 95,9    | 2M <sub>1</sub>                                                     |                                                 |
| 32         | 5,19                         | 8,98 | 20,08 | 95,8    | 2M <sub>1</sub> ; traces of 1M                                      |                                                 |
| 29         | 5,19                         | 8,99 | 20,09 | 95,8    | 2M <sub>1</sub>                                                     |                                                 |
| 670        | 5,19                         | 8,99 | 20,09 | 95,7    |                                                                     |                                                 |
| 25         | 5,19                         | 9,00 | 20,09 | 95,8    | 2M <sub>1</sub> 2M <sub>1</sub> — small admixture                   | Middle Liassic (Pliensbachian)                  |
|            |                              | 8,98 |       |         |                                                                     |                                                 |
| 20         | 5,20                         | 9,01 | 20,07 | 95,7    | 2M <sub>1</sub>                                                     | Same                                            |
|            | 5,18                         | 8,98 | 20,11 | 95,4    | 2M <sub>1</sub>                                                     |                                                 |
| 258        | 5,20                         | 9,01 | 20,07 | 95,8    | 2M <sub>1</sub> 2M <sub>1</sub> — small admixture                   |                                                 |
|            |                              | 8,98 |       |         |                                                                     |                                                 |
| 250        | 5,19                         | 9,00 | 20,07 | 95,8    | 2M <sub>1</sub>                                                     |                                                 |
| 243        | 5,20                         | 9,01 | 20,05 | 95,7    | 2M <sub>1</sub> 2M <sub>1</sub> > 1M; reflections                   | Bezhitin                                        |
|            | 5,19                         | 9,00 | 10,1  | 101     | 1M 02l, 11l diffuse                                                 |                                                 |
| 221        | 5,20                         | 9,01 | 20,10 | 95,8    | Same                                                                |                                                 |
|            | 5,19                         | 9,00 | 10,1  | 101     |                                                                     |                                                 |

Total extinction of clay particles positioned parallel to the bedding can often be seen in thin sections. From among authigenic minerals which arise during the stage of diagenesis, the following are often found: globular pyrite, siderite forming concretions, and, rarely, eggstones of iron chlorite.

Dark gray, often almost black clay slates are abundant in the zone where folding and intensive cleavage occurs, and especially in the Middle Liassic portion; brown tints are absent here. The slates are hard. They ring when struck and can be split into flat pieces along the cleavage planes. The sedimentational fabric in the slates is often obscured by the cleavage and can be recognized only with difficulty. This obscuring effect is revealed in thin sections as cleavage planes in the form of dense, dark bands cutting the rock at an angle to the layering. Thin and elongated leaves of newly formed mica can be seen along these planes. In the slates, one can find segregations of pyrite in the form of regular cubes around which rimlets of authigenic chlorite or quartz have formed.

Comparisons of the argillites and slates shows that these rocks differ significantly. In addition, let us note that between these rocks, representing the end members of a series of clay rocks, transitional varieties exist which have been subjected to postdiagenetic processes to various degrees. The change in the external appearance of the deposits is accompanied by a series of transformations in the mineral composition of the rock.

Characterization of the Clay Minerals. X-ray Investigation of the Samples. In order to determine the phase composition of the <0.001 mm clay-rock fraction, x-rays were made of oriented preparations and powders of these samples with the aid of a DRON-2 diffractometer (Cu K $\alpha$ ). We identified whole-number, or very nearly whole-number series of 00l basal reflections with d(001) = 10 Å (characteristic micaceous minerals) on the diffractograms of

TABLE 2. Chemical Compositions of the Sericitic and Hydromicaceous Phases of the <0.001 mm Fraction, %

| Sample No. | SiO <sub>2</sub> | Al <sub>2</sub> O <sub>3</sub> | TiO <sub>2</sub> | Fe <sub>2</sub> O <sub>3</sub> | FeO  | MnO  | MgO  | CaO  | P <sub>2</sub> O <sub>5</sub> | Na <sub>2</sub> O | K <sub>2</sub> O | H <sub>2</sub> O <sup>+</sup> | H <sub>2</sub> O <sup>-</sup> | C <sub>org</sub> | Σ      | Suite or subsuite from which samples were selected |
|------------|------------------|--------------------------------|------------------|--------------------------------|------|------|------|------|-------------------------------|-------------------|------------------|-------------------------------|-------------------------------|------------------|--------|----------------------------------------------------|
| 287        | 57,56            | 20,57                          | 0,90             | 1,71                           | 0,50 | None | 0,72 | 1,54 | 0,04                          | 0,62              | 5,13             | 5,38                          | 3,03                          | 2,23             | 99,93  | Igatlinsk                                          |
| 44         | 52,82            | 24,30                          | 0,73             | 0,84                           | 0,20 | »    | 0,53 | 1,42 | 0,11                          | 1,35              | 4,58             | 7,08                          | 2,77                          | 1,22             | 97,65  | Upper Toarcian of the monoclinial zone             |
| 51         | 52,89            | 24,52                          | 0,95             | 0,90                           | 0,31 | »    | 0,40 | 1,62 | 0,05                          | 1,05              | 4,85             | 7,93                          | 2,28                          | 1,19             | 98,94  | Middle Toarcian of the monoclinial zone            |
| 37         | 52,53            | 23,74                          | 0,98             | 0,79                           | 0,77 | »    | 0,69 | 1,35 | 0,04                          | 0,49              | 6,32             | 6,84                          | 1,86                          | 1,25             | 97,65  | Middle Toarcian of the zone of box folding         |
| 25         | 53,78            | 28,48                          | 1,12             | 0,83                           | 0,27 | »    | None | 0,56 | None                          | 1,86              | 5,13             | 6,07                          | None                          | 0,72             | 98,82  | Middle Liassic                                     |
| 20         | 53,48            | 28,34                          | 1,11             | 0,72                           | None | »    | 0,18 | 0,32 | »                             | 2,20              | 4,58             | 6,75                          | 0,63                          | 0,83             | 99,14  | »                                                  |
| 258        | 47,19            | 29,71                          | 1,15             | 0,61                           | 0,29 | »    | 0,09 | 1,38 | 0,03                          | 1,86              | 5,54             | 8,33                          | 0,69                          | 2,54             | 99,41  | »                                                  |
| 250        | 54,00            | 25,18                          | 1,04             | 1,57                           | None | »    | 0,19 | 1,24 | 0,02                          | 1,69              | 5,13             | 8,06                          | 0,16                          | 1,83             | 100,11 | »                                                  |
| 243        | 54,95            | 25,00                          | 0,99             | 1,23                           | 0,16 | »    | 0,53 | 1,11 | 0,07                          | 0,84              | 4,90             | 6,32                          | 2,32                          | 1,70             | 99,52  | Bezhitin                                           |
| 224        | 54,54            | 27,70                          | 0,59             | 0,85                           | 0,16 | »    | 0,17 | 1,43 | 0,06                          | 1,20              | 4,85             | 4,41                          | 2,20                          | 0,52             | 98,68  | »                                                  |



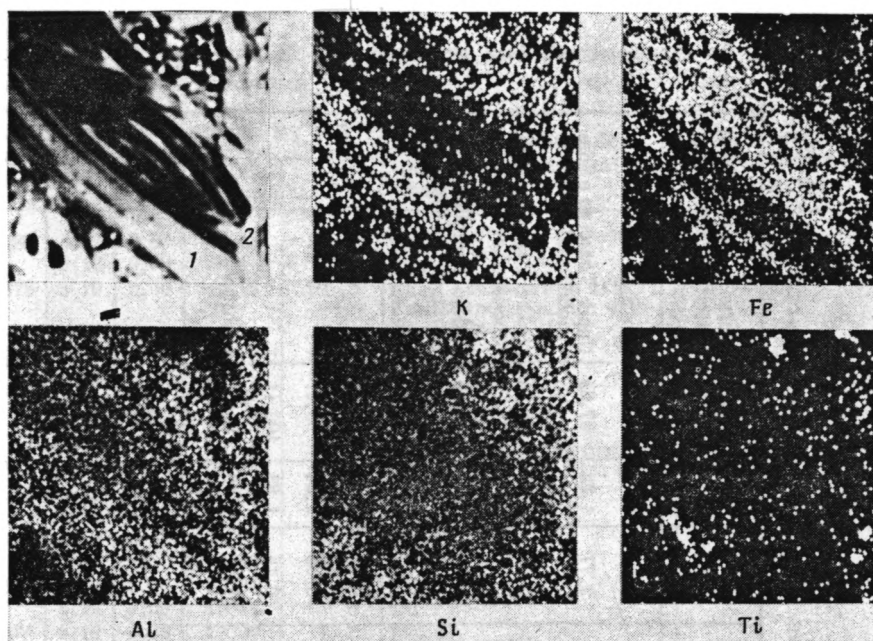


Fig. 6. Distribution of some petrogenic elements in a leaf of hydromica (1) and the chlorite being formed along with it (2). Each side of a photograph represents 200  $\mu\text{m}$ .

natural, oriented preparations. The 002 average reflection with respect to intensity indicates a predominantly aluminum character for the mica. A slight asymmetry in the 001 reflection toward the small-angle side was noted on several of the diffractograms (samples from the upper portion of the section). When preparations were saturated with glycerin, small shifts in the first basal 001 reflection toward the large-angle side were noted in a series of samples. These shifts indicate the presence of swelling layers (2:1) in the micaceous minerals [5]. B. I. Onel'yanenko, et al [14] developed a methodology for determining the percent-content of swelling layers in the micaceous minerals according to the shift in the interplanar distance between the first basal 001 reflection for unadulterated samples and the first basal 001 reflection for samples saturated with glycerin. On the basis of the data obtained in this research, we carried out a determination of the mixed-layer nature of the samples under investigation. Following a classification of micaceous minerals with different contents of swelling layers [14], the micas being investigated were separated into two groups: sericites, containing less than 5% swelling layers, and hydromicas, in which the content of swelling layers varies within the range of 5-10%, reaching 15% in individual samples. Typical diffractograms of oriented preparations are presented in Fig. 5. It should be noted that poly-component admixtures in the following associations were found in practically all of the samples: mica-chlorite (defective chlorite)-quartz, mica-kaolinite-quartz, mica-chlorite (defective chlorite)-kaolinite-quartz. The chlorite content varied from being from the predominant phase (70-50%; samples 25, 673, 677, 678, 680-690) to being a subordinate component (less than 30%; samples 258, 237-242). The parameter for the elementary chlorite cell  $b$  equaled 9.24-9.30  $\text{\AA}$ , with  $d(600) = 1.543-1.549 \text{ \AA}$ . The distribution of intensities for the 001 basal reflections (Fig. 5) indicate a ferromagnesian composition for the chlorites present in the admixtures [10], while the ratio of Fe to Mg varied in different portions of the section. Along with the ordered chlorite in which the interplanar distance  $d(001)$  remained 14  $\text{\AA}$  after heating to 550°C, so-called defective chlorite, in which the interplanar distance  $d(001)$  is shifted from 14 to 12.0-12.5  $\text{\AA}$  was discovered in several samples (samples 48, 267, 272, 274, and 674); quartz was present in subordinate quantities in all the samples.

In several of the samples (samples 43 and 46), kaolinite was clearly identifiable by basal reflections with  $d(001) = 7.15 \text{ \AA}$  in the diffractograms of oriented preparations. In these cases, when kaolinite occurs in admixtures with chlorite, an overlap of the 001 reflections of kaolinite and the 002 reflections of chlorite occurs; identification of the kaolinite is carried out after the chlorite component is removed during the boiling of the clay fraction in a 10% HCl solution.

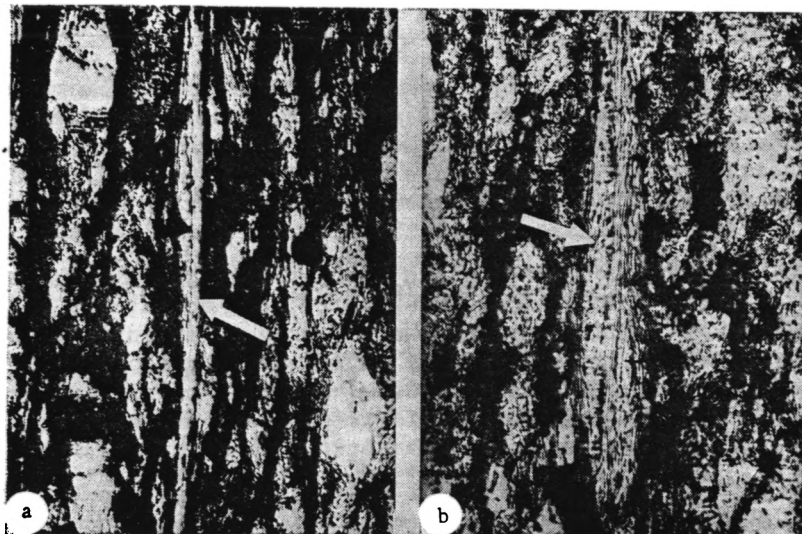


Fig. 7. Cleaved slates (thin section,  $\times 400$ ). Shales: a) clay slates, b) clayey-silty shales. Leaves of authigenic mica lying along cleavage surfaces are vertically positioned at the center; the sedimentational layering is oriented horizontally or at a large angle to the cleavage.

Electron-diffraction Study of the Samples. In order to discover possible differences in the polytypic modifications of the micas and to determine the parameters of their elementary cells, a portion of the samples were studied with the aid of the electron-diffraction method of bevelled textures. All of the samples containing chlorite were subjected to a preliminary treatment for its removal. The studies were carried out on a ER-100 electron-diffraction camera at voltages increasing by 100 kV. During the analysis of the electron-diffraction patterns of oblique texture (EOT) our attention turned to the realization that the numbers of reflections and the distributions of their intensities were different for the different samples on the first ellipse, on which the 02 $\bar{L}$  and 11 $\bar{L}$  reflections ( $k \neq 3n$ ) were located. The interpretation of these EOT allowed us to establish that the samples under investigation were represented by a series of different combinations of micaceous minerals of the 1M and 2M<sub>1</sub> polytypic modifications, the ratio varied from a predominance of 1M micas (samples 44, 46, 287, 678, and 680) through approximately equal concentrations of 1M and 2M<sub>1</sub> micas (samples 20, 25, 29, 32, 37, 51, 250, 258, and 670). The parameters of the elementary cells of the micas are presented in Table 1. Similar EOT were obtained by B. V. Zvyagin during an investigation of mechanical admixtures of micas of the 1M and 2M<sub>1</sub> polytypic modifications.

In the EOT of several samples (samples 20, 25, and 258), two reflections, 060 with  $d_1 = 1.051$  and  $d_2 = 1.496$  Å and reflections with  $k \neq 3n$  (02 $\bar{L}$ , and 11 $\bar{L}$ ) registered clearly; they are somewhat broadened but not decomposed, and their geometric positions and spread of intensities correspond to the diffraction patterns from micas of the 2M<sub>1</sub> polytypic modification. No extraneous reflections were found in the EOT. These data indicate that two phases of mica belonging to the 2M<sub>1</sub> polytypic modification are present in the samples; they differ with respect to chemical composition and result in differing dimensions of the elementary cells.

Segregations of authigenic mica developed along plant remains (leaves and stalks) were noted in one of the samples from the Toarcian deposits within the zone of arched folding. Study of this mica has revealed the high degree of its crystallization:  $d(001) = 9.98$  Å, and the parameters of the elementary cell  $a = 5.20$  Å,  $b = 9.01$  Å,  $c = 19.99$  Å,  $\beta = 95.79^\circ$ . The mica belongs to the 2M<sub>1</sub> polytypic modification.

Distribution of Clay Minerals in the Section and on the Profile. Investigation of the clay minerals from various portions of the section and profile allowed us to uncover fully the regular tendencies in their distribution.

First of all, let us turn our attention to the shift in the association of clay minerals within the deposits of the profile (see Fig. 3). Thus, hydromicaceous-chloritic, hydromicaceous-kaolinitic and mixed hydromicaceous-chloritic-kaolinitic associations of clay minerals are found within the zone of monoclinial bedding. The deposits of the various suites

are basically characterized by their associations. For example, the clay rocks of the coal-bearing Kharakhsk suite have a hydromicaceous composition. In the deposits of the Igatlink suite lying above them, hydromica, chlorite, and defective chlorite are present. It should be noted that this collection of clay minerals is characteristic of the Igatlink suite in another section located 25-30 km to the northeast of the section being described (see Irganai); i.e., it is fairly consistent over the area.

Hydromica and chlorite predominate in the deposits of the Toarcian underlying the Kharakhsk suite and in rocks of the Tsudakharsk suite; but admixtures (and sometimes substantial quantities) of kaolinite occur in some horizons. Kaolinite in packets with large quantities of sideritic concretions completely replaces chlorite (the Upper Toarcian, Sample 43). There is no distinctly expressed predominance of one mineral over the others in the deposits of the monoclinial zone; in individual samples, the chief mineral is chlorite or kaolinite, but hydromica is predominant in other samples.

The relative variety in the collection of clay minerals within the deposits of the monocline changes at the transition to the zone of fold deformations into a singly type of hydromicaceous (sericitic)-chloritic association. Kaolinite was not found in any of the samples analyzed. Sericite and hydromica are the chief minerals here; chlorite predominates only in individual samples. A hydromicaceous-chloritic association is also characteristic of the clayey deposits of the Bezhitin suite.

By examining the character of the hydromica and sericites within the profile, we can see that the number of smectitic layers within these rocks does not remain constant. The hydromicas of the Toarcian and Middle Jurassic deposits of the monoclinial zone usually only contain 5-10% smectitic layers; individual samples may contain up to 15%. Varieties with less than 5% swelling layers can also be found. We did not observe a definite pattern to the changes in the quantities of these layers from top to bottom along the section here. It should be noted that micaceous minerals with similar concentrations of the swelling component are also abundant within the suites. In the argillites of the Igatlink suite, for example, this component makes up no less than 5-10% of the total; individual samples with concentrations of the swelling component less than 5% do occur in the Tsudakharsk suite and also in the Kharakhsk suite, however.

To the south of the monoclinial zone, a pattern of decreasing quantities of swelling layers can be seen as one passes to zones of increasingly more pronounced fold deformation; this takes place fairly rapidly. Thus, sericites with less than 5% swelling component are abundant in the northern portion of the box-fold zone. The swelling component disappears completely in the southern portion of this zone as one approaches the zone of arched folding. Note that a disappearance of micas of the 1M polytypic modification is also noticeable at this same level (somewhat to the south). Non-swelling sericites are abundant within the zone of arched folding and sharply inclined folding.

Within the Bezhitin depression south of the Bokovoi Range anticlinorium, clay rocks occur in which one finds both sericites with <5% swelling layers and also hydromicas with 5-10% swelling layers (in one sample, even 10-15%).

A quite clearly defined tendency can be seen in the changes in polytypic modifications of hydromicas along the section. As is evident from Table 1, there is an overwhelming predominance of the 1M polytype in the very uppermost portions of the profile. A gradual increase in the quantity of the 2M<sub>1</sub> polytype takes place downward along the section. Within the monoclinial zone, this tendency can be traced in relation to increasing age of the rock. In zones of intensified folding, increases in the quantity of the 2M<sub>1</sub> polytype occur in uniformly aged Toarcian deposits according to the degree of crumpling, while only the 2M<sub>1</sub> polytype is found in the most dislocated Toarcian rocks.

In the Middle Liassic series, exposed to maximum crumpling, only sericites of the 2M<sub>1</sub> polytype occur. It is precisely here that the presence of two phases of sericite with somewhat differing parameters for the elementary cell were found in a number of samples from clay slates. An admixture of the 1M and 2M<sub>1</sub> hydromica polytypes (a 2m<sub>1</sub> predominates) is present in the deposits of the Bezhitin suite.

The chemical compositions of sericites and hydromicas from the <0.001 mm fraction are presented in Table 2. It is evident that the transition from Toarcian and Aalenian deposits to Middle Liassic deposits, i.e., from argillites to clay slates, is accompanied by an

increase in the  $\text{Al}_2\text{O}_3$  content in the minerals; an increase in  $\text{Na}_2\text{O}$  and  $\text{TiO}_2$  is less markedly expressed. On the other hand, the quantities of  $\text{MgO}$ ,  $\text{FeO}$ , and  $\text{H}_2\text{O}$  decrease. It is difficult to arrive at a judgement concerning the  $\text{SiO}_2$  content, since there is some admixture of quartz present together with the hydromica and sericite in the samples, and the content of silica in Table 2 reflects the total quantity of this component. As is evident from Table 1, two types of hydromica and sericite exist in practically all the samples; in individual instances, an admixture of the  $1\text{M}$  and  $2\text{M}$  polytypes are present, and in other cases, two phases of the  $2\text{M}$  polytype are present; calculations of crystallochemical formulae are unsuitable in this situation.

Let us turn our attention to the somewhat lowered quantity of  $\text{K}$  in the composition of micaceous minerals when there is a simultaneously increased  $\text{Na}$  content, especially in the lower, Middle Liassic portion of the section. A replacement of a portion of the potassium by sodium apparently occurs, i.e., paragonitization of sericite takes place. In a number of samples, this phenomenon is reflected in a shift in the  $d(001)$  reflection to the high-angle region:  $d$  changes from 10.00 to 9.89–9.90 Å.

In all probability an alteration in the chlorite polytypes similar to those established in other regions [7, and others] takes place in the section in parallel with the alteration of hydromicas. However, the constant presence of hydromica in the samples, interfering with the determination of the chlorite polytypes, did not allow us to carry out the necessary observations in the present report.

In addition to what we have discussed, the x-ray study of the samples allowed us to evaluate the character of the chlorites in different portions of the  $\text{J}_{1-2}$  section. Several x-rays of powder preparations from the clay fractions were obtained for this purpose. A change in the  $b$  parameter of the elementary cell of the chlorites from 9.24 Å for Middle Jurassic deposits (samples 287, 680, and 690) to 9.29–9.30 Å for Middle Liassic deposits (samples 20, 25, and 258) was discovered in the results. The tendency which was uncovered may indicate an increase in the degree of ferruginosity of the chlorites within the section studied from rocks less altered by cata- and metagenetic processes to those more altered. The same x-rays allow us to infer the absence of substantial alterations in the  $b$  parameter of the mica; this is in agreement with the data from the electron-diffraction investigations.

Data obtained during a microprobe analysis of thin sections from clay slates with silty admixtures also suggest a relatively high ferruginosity for the chlorites. The distribution of elements in the micaceous portion and in the chlorite developed along the leaves of the split mica are shown in Fig. 6. A comparison of these distributions shows that there is a significant fall in the concentration of  $\text{K}$ , some decrease in the quantity of  $\text{SiO}_2$ , and a fairly substantial increase in the  $\text{Fe}$  content in chlorite relative to that in mica.

### Discussion of Results

In order to explain the mineral distribution which was brought to light, we should first evaluate how much of an influence the conditions of sediment accumulation and the evolution of the sources of terrigenous drift had upon the distributions.

The geosyncline of the Major Caucasus went through a generally uniform period of development during the Domerian, Toarcian, and Aalenian stages. At this time, we can delineate the following as dividing sutural zones in the Caucasus region: the Skifsk platform, the Major Caucasus geosyncline itself, and the Transcaucasian median mass. At the beginning of the early Bajocian, a shoaling of the marine basin and a growth of rises took place; this led to closure of the troughs and regression of the sea. A new, broad transgression began in the early Bajocian, this ended the general regression at the end of the Bathonian substage with a rising and drying of almost the entire territory of the Major Caucasus and the forelying areas [15].

During the entire time of development of the geosynclinal trough, from its subsidence to its closure, sources of drift, consisting of fragmental material, were generally unchanged: to the north, the Skifsk platform played an important role in supplying material within Dagestan, and the Transcaucasus median mass played an important role to the south. The situation became somewhat complicated during the Bajocian, when a rise was created in the region of the modern Bokovoi Range (its eastern portion). This rise is the Samuro-Shakhdag'sk anticline, which served as a local source of terrigenous material as a result of the scouring of the Middle Jurassic strata which were deposited earlier. Data from a study

of the evolution of the terrigenous-mineralogical provenances of the Northern Caucasus [3] provides evidence that the sources of sedimentary material remained generally unchanged for the entire time of development of the geosyncline, from the Liassic to the Bathonian substage.

On the basis of an analysis of the terrigenous components, V. T. Frolov [17] concluded that metamorphic complexes, granitoids, and also sedimentary and effusive strata which were weakly or generally unmetamorphosed entered into the composition of the distributive provenances. Sedimentary rocks played a more important role in the composition of the denuded lands in Western Dagestan than in Eastern Dagestan. The oligomictic composition of the sandstones indicates that a fairly mature material was supplied to the basin. Weathered crusts apparently developed in the territory of the Hercynian folded structure during conditions of fairly humid and warm climate [16].

In addition, it should be noted that diverse depositional environments were present in the provenances during Early and Middle Jurassic times; the facially diverse types of deposits are evidence of this. A major portion of the series accumulated under open-marine conditions in a basin of normal salinity. At the conclusion of the Late Toarcian-Early Aalenian times, however, formation of deltaic and foreshore-marine deposits of the Kharakhsk suite (predominantly sandy, locally coal-bearing) took place in the territory of the northeastern Caucasus. The northeastern portion of the basin was, at this time, freshened to some degree by the supply of large volumes of water from rivers. To a significant degree, the diversity of depositional environments in the Early and Middle Jurassic basin resulted in appearances of one or another association of clay minerals. Thus, in discussing the distribution of clay minerals in the section, it should be taken into consideration that, on the one hand, constant supplies of sedimentary drift material were present throughout the entire Early and Middle Jurassic times and, on the other hand, that accumulation of sediments took place in various depositional environments. The latter circumstance is responsible, in part, for the observed change in the association of clay minerals within the section of Upper Toarcian-Middle Jurassic deposits. However, although changes in depositional conditions may have had a significant effect upon the presence or absence of chlorite or kaolinite (fragmentary or diagenetic), hydromica (sericite) remained a constant component and is relatively equally distributed along the section. Solving the problem of what the hydromicas consisted of during the stages of sedimentogenesis and diagenesis is complicated. Participation of sandy-clayey deposits in the formation of the northern pre-Jurassic dry land would inevitably lead to a drift of fragmental micaceous minerals into the basin. Moreover, the volcano-sedimentary Triassic stratum being scoured would result in the appearance of montmorillonite in the sediments of the basin. The montmorillonite would pass through a further series of mixed-layer minerals (during catagenesis) to become hydromica. In this connection, it is interesting to note that Ch. M. Khalifa-Zade and A. M. Magonedov [18] noted the presence of montmorillonite, which they associated with volcanogenic material, in a single sample from the Bajocian deposits in the Aivar Koisu River valley.

Judging from the invariance of the sources of sedimentary material and also taking into account the fact that hydromica of the 1M polytype predominates in the upper portion of the terrigenous  $J_{1-2}$  section most subjected to the action of catagenetic processes, one can fairly confidently assume an initially wide (predominant) distribution of this polytype over the entire stratum of the Liassic and Dogger. The change in polytypic modifications of the hydromicas established in the section, the disappearance of smectitic components and the transition of the hydromicas to sericites, the improvement of their crystallization, and some alterations in chemical composition (an increase in Al content, a decrease in  $H_2O$ ,  $MgO$ , etc.) should be connected with an increase in the cata- and metagenic reworking of the deposits. The transition of the 1M polytype of the hydromicas to  $2M_1$  and the other alterations of these hydromicas during the process of burying the strata at great depths has been demonstrated for various regions [7-12, etc.]. A final disappearance of kaolinite, which is fairly widely occurring in the rocks of the upper portion of the section, can be seen simultaneously with alterations of the hydromicas in the Middle Jurassic deposits of the monoclinical zone and in all of the dislocated strata south of it. This phenomenon is characteristic of deposits which have undergone intense reworking of material [12 and others].

The tendency noted in the  $J_{1-2}$  Dagestan section for an increase in ferruginosity at the transition from argillites to clay slates does not coincide with what has been observed in other regions [7, 11, 13, and others], and is apparently due to specific postdiagenetic processes in the terrigenous strata of the Caucasus. Note that Zh. Millo [12] has pointed

out the possibility of a redistribution and incorporation of  $\text{Fe}^{2+}$  into the structure of chlorite within zones of high temperature and pressure.

One of the chief factors exerting appreciable effects on the postsedimentational transformation of rock is the pressure created by the weight of the overlying sediments. It can be said with some certainty that the Middle Jurassic deposits are overlapped by Upper Jurassic and Cretaceous strata, which amount to 3100-3750 m in total thickness ( $J_3$ , 1000,  $C_1$ , 900-1200, and  $C_2$ , 1200-1500 m). At the present time, there is no definite evidence of an accumulation of deposits younger than the Cretaceous within the modern area where the Lower and Middle Jurassic deposits occur. On the other hand, the existence of remnants of thin Middle and Upper Miocene deposits lying upon Cretaceous rocks (i.e., the entire Paleogene and Lower Miocene have been dropped from the section) within calcareous Dagestan to the north of the section studied most likely indicates a stable rise of the axial portion of the Major Caucasus in post-Cretaceous time.

Taking into account that the thickness of the  $J_{1-2}$  section has been estimated to be approximately 9 km (Fig. 2) and that the thickness of the overlapping deposits is more than 3 km, the most ancient Liassic horizons exposed at the present time by erosion have subsided to a depth of approximately 12 km.

However, it is only possible to connect changes in the sedimentary rock with normal geostatic loading within the deposits with monoclinial bedding, i.e., approximately up to the lower horizons of the Upper Toarcian stratum within the exposed portion of the section, since to the south, where more ancient strata are uncovered, traces of the effects of lateral stress upon the rocks have already begun to reveal themselves. The depth of burial of the lower portion of the Upper Toarcian stratum is estimated to be 7.5-8 km.

The tendency for a transition of  $1M$  hydromica polytypes to  $2M_1$  within the monocline has already been established. Since a gradual change of one polytype to the other takes place without microscopically visible alteration in the primary material of the clay rocks, it is, in all probability, possible to consider the  $2M_1$  hydromica which appears as being basically transformational.

The lateral stress manifesting during the time of folding was a powerful factor in the transformation of the deposits. The cleavage arising during this time had an effect upon the physicomaterial properties of the rock, causing a reorientation of the rock's components and frequently entailing a partial recrystallization of the material. This is evident in Fig. 7, where the cleavage planes literally pierce the clay slate. The dark coloration of the bands is due to grinding of the original clayey material. In addition, one frequently encounters thin and elongated leaves of newly formed mica along the bands (Fig. 7a, b); these arise as a result of rubbing of the material. Authigenic mica formed during the stage when the cleavage developed or immediately after it can be quite clearly identified. The appearance of two phases of the  $2M_1$  polytype (see Table 1, samples 20, 25, 258) should be connected with the presence of two types of mica in the rock, transformational and authigenic mica.

Finally, the temperature factor played an important role in the transformation of the rock. Unfortunately, there are no data allowing us to establish the degree to which the strata were heated; however, rough calculations indicate that the most ancient Middle Liassic deposits were subjected to the effect of temperatures reaching  $280^\circ$  and above.

An increase in the degree of cata- and metagenic alteration of the rock along the a profile studied is reflected in other components of the deposits besides the clay minerals. The organic matter is indicative in this regard: the reflectivity of vitrinite varies over a wide range within the section. Thus, the rocks of the Kharakhsk suite (the upper portion of the section) contain plant remains and coaly interbeds with  $R^\circ$  values which reach 1.12-1.15. This corresponds to the end of the veined-coal stage and the beginning of the coke stage associated with the reworking of the material. In the region where cleaved Middle Liassic slates occur, the  $R^\circ$  values are significantly higher (up to 8-8.5); i.e., the degree of alteration of the organic matter reached the anthracite stage. The alteration in the coloration of the rock from the brownish-gray of the argillites in the Middle Jurassic to the dark-grey and black of the slaty slates in the Liassic is connected with the increasing degree of metamorphism of the organic matter.

The physical properties of the rocks also change along the section. The specific gravities of the rocks in deposits of monoclinial zone vary over a range of 2.5-2.6 g/cm<sup>3</sup>. There are more altered rocks in the lower portion of this section, in the Middle Liassic. The specific gravities of the rocks reach 2.7 g/cm<sup>3</sup> here and sometimes 2.72 g/cm<sup>3</sup>.

The metagenetic reworking of the clay rocks also affected the mineral composition of the diagenetic concretions within the rocks. The siderite component within the concretions became unstable and was replaced metasomatically by other minerals. Peculiar nodules composed of fine-grained rock consisting of quartz and chlorite, often with abundant disseminations of pyrite formed by iron from disintegrating siderite, were created as a result [2]. This tendency can be easily traced in horizons of coeval deposits extending from the zone of monoclinally bedded layers into the region where intensive dislocations and cleavage are present.

We suggest that the Durans basin in the Alps [20] is the geological situation most similar to ours from among those which have been studied thus far. The Jurassic strata occurring in this area were subjected to the effects of geostatic pressure during burial and, principally, processes connected with alpine orogenesis. Many of the tendencies in the alterations of the clay minerals discovered here are essentially the same as those found in the Lower and Middle Jurassic deposits of Dagestan.

From the data presented above, it is evident that the Lower and Middle Jurassic strata have experienced intensive postdiagenetic transformations manifested with varying intensities in different parts of the strata. If the upper portion of the strata, overlapped by younger deposits, subsided to a depth of 3-3.5 km, then the oldest horizons were buried to 12 km or more. Geostatic load, elevated temperature, and further lateral stress acted upon the rocks in this case. As far as the stages of lithogenesis are concerned, the roof of the stratum corresponds to the approximate boundary between the middle and late catagenesis, but the Middle Liassic deposits reached the stage of late metagenesis. Although we uncovered the general direction of the changes in the clay minerals within the stratum studied, several aspects of the dynamics of the transformations of these minerals remain unclear thus far, in particular, the character of the transitions of individual minerals into other minerals, the scales of these processes, the gradualness or discreteness of the transformations, and questions concerning the times of the alterations of different minerals with respect to the stages of metagenesis.

In addition, the material we have presented allows us to now estimate the times of several transformations in the Dagestan section of the Jurassic stratum. Thus, the disappearance of kaolinite occurs in the lower portion of the section of the monoclinial zone; this corresponds to the concluding stage of late catagenesis. The transition of the hydro-mica from the 1M polytypic modification to the 2M<sub>1</sub> took place gradually over the entire J<sub>1-2</sub> stratum, i.e., throughout the duration of the entire late catagenesis, and finished with a complete transition to the 2M<sub>1</sub> polytype during the stage of metagenesis. It should also be noted that small quantities of smectitic packets (a few percent) were preserved in the sericites for a fairly long time and finally disappear only in the zone where the material was reworked metagenetically.

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A COMPARATIVE ANALYSIS OF DISINTEGRATION METHODS  
FOR PALEOSTRUCTURE GRANULOMETRY IN UPPER JURASSIC SANDSTONEST. G. Egorova, A. V. Ezhova,  
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UDC 552.08.53:552.51:551.762

Granulometric sample analysis is necessary for paleographic reconstructions. Sieve analysis is the simplest and most economical of all forms of granulometric sample analysis. It is acknowledged [1] that sieve analysis gives accurate results for rocks that are easily disintegrated into their component parts. For analysis of more durable rocks, the aggregates or cemented particles are broken down by grinding, by boiling in water or a weak solution of HCl, by crushing in a mortar, and by the effect of ultrasound [1-3]. All of these sample preparation methods are protracted, and they introduce specific errors into the resulting analyses. The most acknowledged time-consuming method in durable rocks for grain-size determination, by thin sections, is also not free from error [1].

Our purpose was to obtain original data for the creation of a unified procedure for the preparation of sedimentary rock samples for estimation of granulometric composition. This would guarantee reduction in labor costs and preservation of the natural forms and sizes of the constituent grains. We conducted comparative trials on sample disintegration of sedimentary rocks: by manual disintegration (in a porcelain mortar) and by the electroimpulsive method (EI) in the crushing-pulverizing complex CPC-1. The foundations and applications of the EI method for the disintegration of hard bodies are found in a series of articles [5-8].

We conducted trials on 40 core samples of sedimentary rocks of the Western Siberian region from five wells. Each sample was divided into two parts. The samples were represented by grey fine- and medium-fine-grained solid sandstone, with thin interlayers of clay, carbonaceous, and micaceous material, poor sorting of grains with diameters of 0.1-0.8 mm, and cement content from 10 to 40%. The samples were represented by lumps with linear sizes up to 70 mm. Half of the sample mass, from 80-500 g, underwent manual crushing, which was carried out in a porcelain mortar by simple vertical strokes of the pestle with periodic screening of material through a sieve with meshes of 1 mm. The product was considered to be prepared when it passed through the sieve. The planned time for manual crushing of a 500-g sample took 1 h [4].

Electroimpulsive crushing was conducted in industrial water by single impulse parameters [7] on a perforated grounded electrode with meshes equal to 1 mm (the electrode diameter is 15 cm, the volume of the cylindrical chamber is 3 liters). The time for sample disintegration did not exceed 4 min. The prepared product was collected in a receiving bin. After pulverizing, the samples clotted, the water was discarded, and the product was dried at a temperature no greater than 100°C.

The samples pulverized in the mortar and in the EI-crusher were then processed in similar manners: boiling in water, careful wiping away of the wet sample by a rubber pestle, washing off of the <0.05-mm fraction on the sieve, drying of the >0.05-mm fraction and sieving into narrow classes, control of the granular material under a binocular and its finishing into monofractions by sieving, and pipette analysis of the <0.05-mm fraction [2].

In Fig. 1a, for example, curves are shown of the distribution of granulometric composition for products of manual and EI-crushing for sample 147 from well 23 of the Northern Kalinov area. A similar pattern, which shows some redistribution of the resulting quantities of the fractions, with preservation of the general form of the curve and close values of the granulometric coefficients, is characteristic of the investigated samples from wells 23 and 10 of the Nizhnetabagansk area, well 23 and 50% of the samples from well 30 of the Northern Kalinov area, and 70% of the samples from well 22 of the Kalinov area.

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Tomsk Department of SNIIGGiMS. Translated from *Litologiya i Poleznye Iskopaemye*, No. 1, pp. 129-131, January-February, 1987. Original article submitted February 18, 1986.

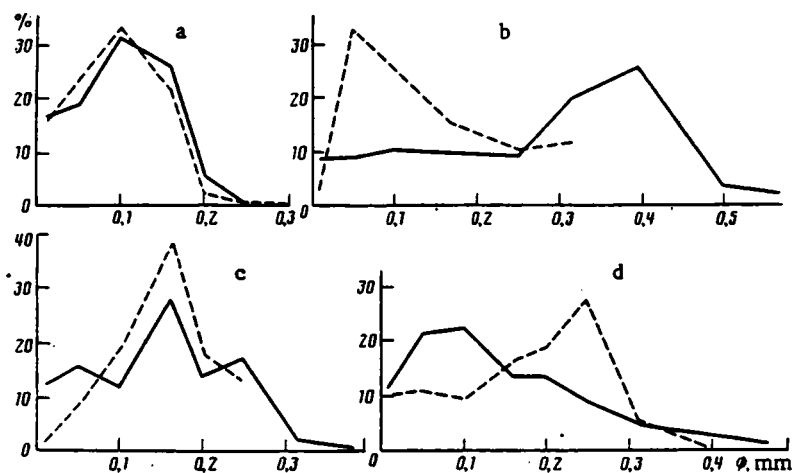


Fig. 1. Curves of the distribution of the granulometric composition in samples obtained by manual (solid line) and electroimpulse (dashed line) crushing methods. a) sample 147 from well 23 of the Northern Kalinov area; b) samples 15 and 16 from well 30 of the Northern Kalinov area; c) samples 29 and 30 from well 1 in the Nizhnetabagansk area; d) sample 96 from well 22 of the Kalinov area.

TABLE 1. Output of Monomineralic Grains, %

| Sample number | Grain diameters, mm |           |           |           |           |           |           |
|---------------|---------------------|-----------|-----------|-----------|-----------|-----------|-----------|
|               | 0.50+0.40           | 0.40+0.30 | 0.30+0.25 | 0.25+0.20 | 0.20+0.16 | 0.16+0.10 | 0.10+0.05 |
| 141           | —                   | 32,0      | 56,0      | 82,8      | 93,4      | 100       | 100       |
|               | 80,0                | 84,0      | 88,6      | 95,8      | 95,8      | 100       | 100       |
| 147           | —                   | —         | —         | 82,0      | 84,0      | 85,0      | 97,0      |
|               | —                   | 90,0      | 95,2      | 93,0      | 92,7      | 93,0      | 100       |
| 150           | —                   | 5,4       | 4,8       | 5,4       | 36,1      | 65,4      | 82,1      |
|               | —                   | —         | 32,0      | 29,0      | 37,0      | 76,1      | 90,0      |

Note. Manual crushing results are shown in the numerator, the results of electroimpulse grinding are shown in the denominator; dashes denote "lack."

For 50% of the samples from well 30 of the Northern Kalinov area, and 20% of the samples from well 22 of the Kalinov area, we observe not only redistribution of the resulting quantities of the fractions in the pulverization products, but also change in the form of the curves which is similar to that presented in Fig. 1b for samples 15 and 16 from well 30 of the Northern Kalinov area.

A sharp difference in granulometric characteristics is only determined for two samples (29 and 30) from well 1 of the Nishnetabagansk area; with EI-crushing the 0.05 mm fraction predominates (see Fig. 1c), with manual crushing the 0.4-mm fraction predominates, while on the other hand, for samples 96 from well 22 of the Kalinov area with EI-crushing the 0.25-mm fraction predominates, while with manual crushing the 0.1-mm fraction predominates (see Fig. 1d). The values of the sorting coefficient and the average grain size also vary significantly.

Grains in products of EI-crushing are significantly more pure than grains in the products of manual crushing, and they are characterized by a smaller number of angular fragments. This is confirmed by results of determining the output of monomineralic grains, which was conducted for well 23 of the Northern Kalinov area (Table 1). The fraction -0.05+0.01 mm merits particular attention. The products of manual crushing contain from 40 to 60% splintered grains which appear in the process of finishing the products to monofractions. In the EI-crushing products, this quantity comes to 7-14% of the content of the material in the frac-

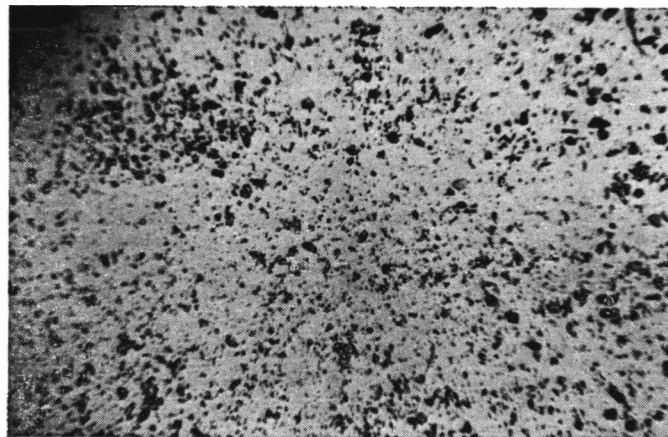


Fig. 2. Form of grains of the fraction  $-0.05+0.01$  mm in a sample of manual crushing.  $\times 50$ .

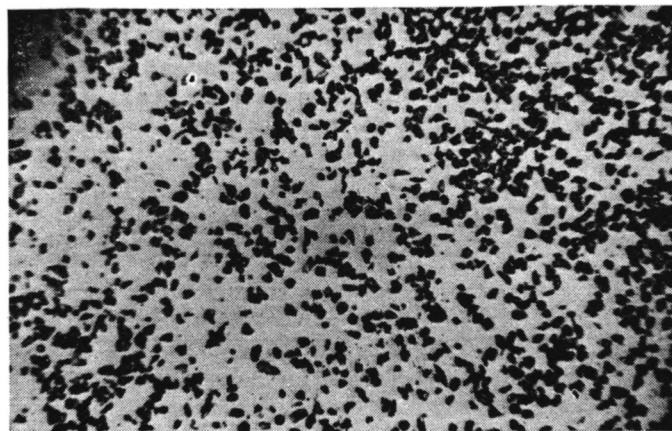


Fig. 3. Form of grains of the fraction  $-0.05+0.01$  mm in a sample of EI-crushing.  $\times 50$ .

tion. The form of the grains of this fraction in the manual crushing product is shown in Fig. 2, while the form of the grains in the EI-crushing product is shown in Fig. 3. Thus, in the manual crushing sample, more than 50% of the grain splinters in this fraction have an average diameter of 0.014 mm, while in the EI-crushing samples, there are less than 10%; the grains are uniform in size, with an average diameter of 0.04 mm. This increases the accuracy of sieve analysis with EI-crushing.

Mineralogical analysis of sample 150 from the Northern Kalinov area showed that it had a large pyrite content, with pyrite performing the role both of cement and groundmass. An anomalous yield of the 0.4-0.315 mm fraction is observed in manual crushing. The yield of pure grains in this fraction comes to 5.4% (see Table 1). Fairly good grain separation is observed in the 0.16-0.1 mm fraction.

For a selected initial pulverization coarseness of 1 mm, no yield of the 0.4-0.315 mm fraction is noted after electroimpulsive pulverization, while the 0.2-mm fraction matches the yield obtained from the manual pulverization sample. The quantity of pure grains in the 0.315-0.2-mm classes is approximately 30%, which is 6 times greater than in the manual pulverization trials.

Thus, utilization of the electroimpulsive pulverization method may be promising for the preparation of sedimentary rock samples for granulometric analysis. The cited results show that for the foundation of this proposition it will be necessary to conduct further investigations, with inclusion for comparative purposes of data on the determination of the granulometric composition in thin section. In addition, comparative mineralogical analysis of the obtained fractions (particularly the fraction smaller than 0.1 mm) may show if pulverization of quartz grains occurs during electroimpulse disintegration.

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